A TREATISE ON

QUANTITATIVE INORGANIC ANALYSIS

ANALYSIS

WITH SPECIAL REFERENCE TO THE ANALYSIS OF
CLAYS, SILICATES AND RELATED MINERALS.

BY

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AND

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A TRIBUTE.

By Sir Robert Robertson, K.B.E., M.A., F.R.S.

Dr. Mellor, a pioneer in the Silicate Industries and a man of unusual mental attributes, has passed away shortly after his retirement, though he was active in the revision of his literary work until the last.

By his investigations, papers and advice as Director of Research, he has greatly advanced the study and practice of Ceramics and especially of Refractories in this country.

By his text-books, embodying personal experience of analytical methods, he has placed in the hands of chemists works which are in daily use at the bench, and in his *Comprehensive Treatise* he has covered the whole field of Inorganic Chemistry in a series of volumes that are a monument to his industry, and a constant and valued source of information to chemists.

The loss of this great exponent of Inorganic Chemistry will be deeply felt not only by those who enjoyed his personal friendship, but by that vast army of students and workers who will remain indebted to his genius as a teacher and writer.

July, 1938.

PREFACE.

In the preface to the first edition I explained that this book evolved from a special course of lectures on the Ceramic and Silicate Industries given about 1910, but that as the work of compiling it developed, it was thought best to segregate the analytical part from the purely ceramic section. In course of time the former was published as the first edition of this treatise.

In the first edition the book was divided into five parts. Some general analytical processes were described in Part I; the analysis of a typical silicate was discussed in Part II; the methods to be adopted with more complex silicates—glazes, enamels, colours, etc.—were indicated in Part III; Part IV showed the modifications required when some of the more difficult, as well as some of the rarer, elements were present; while the last part—Part V—indicated the methods to be employed when acidic elements had to be determined; finally a chapter on the so-called "rational analysis" concluded the volume. The general scheme of the work has been preserved in preparing this new edition.

The methods for the analysis of a typical silicate detailed in Part II are based largely on the classic investigations of W. F. Hillebrand of the U.S. Geological Survey. These methods, although probably the most accurate, do not allow analyses to be conducted with that speed required in certain industrial work, and accordingly I have purposely indicated the short-cuts available to those who have mastered the general methods.

At the time of the publication of the first edition the descriptions of the more common analyses must have been verified at the bench by a score of different workers; but since then a considerable amount of new knowledge has become available, particularly in regard to new reagents and quicker methods of analysis. An endeavour has been made to incorporate much of this in the new edition.

There have been many urgent calls for a new edition and, at last, finding myself unable to prepare a new edition of this work, I was fortunate in being able to persuade Mr. H. V. Thompson, M.A., of the North Staffordshire Technical College, Stoke-on-Trent, to undertake the task. He has had an extensive experience in the subject and I very much admire the thoroughness with which he has overhauled the original work.

Grateful acknowledgements must be made to Messrs C. D. Littler and A. J. Shorter, B.Sc., for the time and care they have given to reading the proofs.

J. W. MELLOR.

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  Portsmouth Road,
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      May, 1938.

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INTRODUCTION.

The Subdivisions of Analytical Chemistry.

Qualitative and Quantitative Analysis.—The general purpose of analytical chemistry is to find the chemical nature of a given material. With simple substances this is comparatively easy, for the object of the analysis is easily attained by establishing the identity of the given substance with one whose properties are known. A simple inspection of the consistency, colour or smell may suffice; in other cases, the specific gravity, boiling-point or freezing-point may have to be determined; and finally, it may be necessary to prepare derivatives of the given substance, and compare their properties with those of known compounds. Thus arise the so-called *tests* of qualitative analysis. On the other hand, if the substance to be analysed be not simple, but is a more or less complex mixture of several simple substances, the analytical operations are more intricate, for the properties of the different components in the complex may be masked by the mere presence of the others so as to render identification almost impossible. In that case, the complex must be resolved into simpler substances which can be separately identified.

If the purpose of the analysis be merely identification, the operations are said to be *qualitative*; while if the amount of one or more of the constituents has to be determined, the analysis becomes *quantitative*. There is a large number of manuals on qualitative analysis in which an elaborate general scheme—now many years old—is described for the identification of the constituents of the most complex inorganic mixtures. In many cases, this scheme is only of pedagogic interest, because, in practice, we generally have a good idea of the components of a mixture, and only the amounts of the more important of these are industrially important. Hence, although a qualitative analysis should precede the quantitative, yet numerous quantitative analyses are made without the preliminary examination, because the qualitative composition of the given substance is well enough known. On the other hand, W. F. Hillebrand has said that, in mineral and rock analyses, the custom of neglecting to make the preliminary qualitative tests is the prime cause of many gross errors.

Gravimetric Analysis.—In gravimetric analysis, the several constituents are separated and weighed or, if they cannot be separated or if they are unsuited for weighing, they are converted into compounds of known composition which can be satisfactorily weighed. The several steps in the operation are:

(1) A definite amount of the substance to be analysed is weighed.

(2) The weighed sample is brought into solution.

(3) The constituents to be determined are separated from the solution, one by one, in the form of definite insoluble compounds, either by precipitation or by electrolysis—*electro-analysis*.

(4) A compound so separated is freed from adherent liquids and solids by filtration and washing.

(5) The compound is dried and ignited so as to convert it into a stable pure compound.

(6) The compound is weighed.

(7) The amount of the substance to be determined is computed by known arithmetical processes from the weight of the ignited compound.

Volumetric Analysis.—In volumetric analysis, the quantity of a constituent in a given solution is determined by adding a sufficient volume of a *standard solution*—containing a known amount of a selected reagent—to produce a definite "complete" reaction. The number of operations involved in a gravimetric analysis is here much curtailed; as a rule, no filtration or washing is needed; nor is any weighing required after the sample has been brought into solution. The operations are:

(1) A definite quantity of the substance to be analysed is weighed.

(2) The weighed sample is brought into solution.

(3) The standard solution of the selected reagent is added until the whole of the substance to be determined has been converted into a definite compound. The completion of the reaction is indicated by a change in the colour of the solution, frequently tinted with a selected dye called the *indicator*.

(4) The quantity of the standard solution required to complete the reaction enables the amount of the substance under investigation to be computed by known arithmetical processes.

Gasometric Methods of Analysis.—If the substance being analysed gives off a gas when it is treated with a selected reagent, such that the volume of gas liberated bears a definite relation to the amount of the constituent in question, the measurement of the volume of the liberated gas, or a determination of the loss of weight which occurs when the gas is all expelled, enables the amount of the constituent to be computed by arithmetic.

Physical Methods of Analysis.—There are several so-called physical methods of analysis in which the variation of some property—say, specific gravity—is proportional to the amount of the substance under investigation which is present in a given mixture. A determination of that property enables the amount of the substance to be computed. In *colorimetry,* for instance, the substance under investigation can be made to produce a coloured solution such that the intensity of the colour varies with the concentration. A comparison of the tint of a known volume of the solution with that of another solution containing a known quantity of the same substance as that under investigation, enables the amount of the given constituent to be computed by simple arithmetic. In *turbidimetry,* instead of comparing the colours, the degree of opacity of the two solutions is compared. This process is of limited application and is only possible when the solution under investigation can furnish a fine-grained solid precipitate which settles very slowly.

The Birth of Analytical Chemistry.

The chemists of the phlogiston period, *e.g.* Basil Valentine, O. Tachenius, F. Hoffmann, A. S. Marggraf and C. W. Scheele,[1] made a large number of

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[1] B. Valentine, *Chymische Schriften,* Leipzig, 1769; O. Tachenius, *Hippocrates Chemicus, qui novissimi salis antiquissima fundamenta ostendit,* Venetiis, 1666 (English trans., London, 1677); F. Hoffmann, *De Methodo Examinandi Aquas Salubres,* Leyden, 1708; A. S. Marggraf, *Chymische Schriften,* Berlin, 1761-7—"Method of reducing silver chloride without loss," 1749; "Chemical examination of water," 1754; C. W. Scheele, *Opuscula Chemica et Physica,* Lipsiæ, 1788-9.

isolated observations which enabled many inorganic substances to be distinguished from one another. Robert Boyle,[1] about 1661, styled the process of identification an *analysis*. About a century later, Bergman [2] compiled and arranged the different tests in a systematic and methodical way and thus laid a foundation upon which Berzelius and Rose [3] built a system of qualitative analysis which has persisted with remarkably few changes up to the present day.

The earliest writings on metallurgy show that from remote antiquity metals have been extracted by heating their ores with appropriate fluxes and there can be little doubt that laboratory methods for the dry or fire assay [4] of ores were modelled upon metallurgical operations conducted upon a large scale. For instance, the so-called Cornish process for the assay of copper [5] is conducted on very much the same lines as that which has been employed for the extraction of copper from its ores for thousands of years and the origin of the method of separating silver from lead by cupellation cannot be traced, because it is alluded to by early writers,[6] *e.g.* Diodorus, Strabo, Suetonius, Pliny, as an old and familiar process.

Bergman's Work.—T. Bergman's brochure upon "the analysis of minerals in the wet way" was published in 1780. In this important essay, Bergman pointed out the existence of errors in dry or fire assaying processes due to such causes as the incomplete attack of the minerals by the fluxes and to the retention of some of the metal by the slag, and he advocated several wet processes in preference to the dry methods of analysis then in vogue.[7] Bergman [8] showed that the amount of a substance in solution was best determined by converting it into a definite compound of known composition and subsequently deducing the amount of the desired constituent from the weight

[1] R. Boyle, *The Sceptical Chymist*, Oxford, 1661; *Experiments and Observations upon Colours*, London, 1663.

[2] T. Bergman, *Opuscula Physica et Chemica (De Minerarum Docimasiâ Humidâ)*, Holmiæ, 1780.

[3] J. J. Berzelius, *De l'Analyse des Corps inorganiques*, Paris, 1827; H. Rose, *Handbuch der analytischen Chemie*, Berlin, 1829.

[4] The term *assaying* is applied more or less vaguely to methods of chemical analysis which are confined to the determination of the commercially important constituents in given materials. Thus, processes for the assay of vegetable products, drugs, ores and alloys, are described in current literature. The assay of ores, alloys and related products can be conducted by treating the material under investigation with suitable solvents so as to get the desired metal into a solution from which it can be subsequently precipitated—*wet or solution processes*; or the given material may be fused with a suitable flux so that the desired substance is reduced to the corresponding metal, which collects as a button at the bottom of the crucible and the associated substances can be separated in the form of a fusible slag— *dry or fire processes.*

[5] M. L. Moissenet, *Ann. Mines*, (5), 13, 183, 1858.

[6] Thus, in the second century B.C., Agatharchidas of Cnidos described the method used by the Egyptians for purifying gold and this resembles the cupellation process for separating silver and lead. C. S. Pliny, *Naturalis Historiæ*, Venetiis, 33, 44, 1472; 34, 48, 1472; G. Agricola, *De Re Metallica*, Basiliæ, 1546 (English trans., London, 1913); A. Libavius, *Ars probandi Mineralia*, Francofurti, 1597; A. Libavius, *De Judicio Aquarum Mineralium*, Francofurti, 1597. The two last-named essays are usually stated to be the first books specially devoted to the analysis of minerals. The first-named is considered to be largely compiled from Agricola's book. See also G. Chesneau, *Revue scientifique*, (5), 3, 321, 357, 1905.

[7] A. P. T. Paracelsus (*Opera Omnia Medico-Chemico-Chirurgica*, Geneva, 1658) is generally credited with having first described an analysis in the wet way. To analyse an alloy of gold and silver, Paracelsus treated the sample with nitric acid—*aqua fortis*—which dissolves the silver and leaves the gold behind in the form of an insoluble black powder. He then precipitated the silver by inserting a plate of copper in the solution. The copper is at the same time vigorously attacked by the free acid.

[8] T. Bergman, *Opuscula Physica et Chemica (De Minerarum Docimasiâ Humidâ)*, Holmiæ, 349, 399, 1780.

of the compound so prepared.[1] Thus lime was weighed as oxalate or sulphate; lead as sulphate or sulphide; sulphuric acid as barium sulphate; silver as chloride although, previous to this, Marggraf [2] had determined the amount of silver in alloys by separating the silver as an insoluble chloride. Bergman recognised that "the sum of the weights of each of the constituents in an analysis should be equal to the weight of the mineral analysed, allowing for a certain loss during the manipulations," and his analysis of a sample of pure gypsum is singularly good, e.g.:

	Vitriolic acid.	Calcareous earth.	Water.
Bergman's analysis .	46	32	22 per cent.
	Sulphur trioxide, SO_3.	Lime, CaO.	Water, H_2O.
Modern analysis . .	46·5	32·5	21·0 per cent.

Bergman also introduced the method of decomposing silicates by fusion with alkali carbonates, and his little treatise, *De Minerarum Docimasiá Humidá*, is thus considered to have inaugurated a new era in analytical practice. It is interesting to note that Bergman felt the great need for a suitable vessel for opening-up his minerals by fusion. He used iron dishes and also Hessian crucibles, but he recognised their imperfections. He tried to make platinum crucibles but succeeded in making only little ones, too small for his purpose. The difficulty in melting the platinum restricted his efforts, so that he could only say: "If they can ever be obtained of proper size, they will be in all respects the best." To-day we should not like to contemplate working without them.

Klaproth's and Vauquelin's Work.—The next advances were made by Klaproth [3] and by Vauquelin.[4] These workers introduced many improvements in technique and analysed many minerals. Klaproth, for instance, ignited his precipitates before they were weighed in cases where the ignition was not attended by decomposition. Quantitative analysis was greatly stimulated by the need for separating the different constituents of the minerals from one another during the many investigations on the composition of minerals made about that time. As Klaproth expressed it: "Nature, inexhaustible in her riches, has intended to keep in activity the ardour of the naturalist in the examination of mineral substances." As early as 1808, we can recognise the beginnings of the present-day method of conducting silicate analyses in John's book,[5] which summarised the labours of Bergman, Marggraf, Klaproth and Vauquelin.

Berzelius' Work.—About 1827, Berzelius [6] took up the work, and considerably advanced the art by devising a number of new methods for the determination and separation of many elements and testing those then in use; Berzelius also introduced a number of improved methods in manipulation: e.g., the hydrofluoric acid process for decomposing silicates; the separation of precipitates by filtration through "filter-paper," followed by subsequent ignition; and, by using small quantities of the material to be analysed, he reduced the errors of manipulation, because small precipitates are more readily cleaned than large ones. Berzelius' pupils, F. Wöhler and H. Rose, worked up the

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[1] In 1755, J. Black (*Experiments on Magnesia Alba, Quick-lime, and other Alcaline Substances*, Edinburgh, 1777; *Alembic Club Reprints*, No. 1, 16, 1893) determined the amount of calcined magnesia in a solution by the addition of sodium carbonate and weighing the resulting precipitate.

[2] A. S. Marggraf, *Mem. Akad. Wiss. Berlin*, 16, 1749.

[3] M. H. Klaproth, *Beiträge zur chemischen Kenntniss der Mineralkörper*, Freiberg, 1795.

[4] L. N. Vauquelin, *Scherer's Journ.*, 3, 410, 1799.

[5] J. F. John, *Chemische Laboratorium*, Berlin, 181, 1808.

[6] J. J. Berzelius, *De l'Analyse des Corps inorganiques*, Paris, 1827.

experience of their teacher with their own in two books: H. Rose's *Handbuch der analytischen Chemie*, Berlin, 1829, and F. Wöhler's *Praktische Uebungen in der chemischen Analyse*, Göttingen, 1853. The later editions of these books are consulted even to-day. About this time also appeared the first edition of Fresenius' famous book (1846), and this was followed by the founding of the *Zeitschrift für analytischen Chemie* in 1862. Thus the modern practice of the art is linked with that of its founders.

Some Uses of Analytical Chemistry.

The information which the analysis is expected to give, as indicated on pages 239–40, determines the method by which it is to be conducted. The information required may be purely of scientific interest, or it may be essentially practical. The utility of analyses for purely scientific purposes need not be here scrutinised. It would be easy to quote many examples where analysis has thrown a new light on the aspect of chemistry.[1] Analysis is an indispensable auxiliary to the mineralogist for, as C. R. Fresenius (1875)[2] has said, it teaches him the true nature of minerals and suggests to him principles and rules for their recognition and classification. H. S. Washington (1903),[3] too, says that analyses are no longer ornamental adjuncts, but essential parts of most petrological publications, on which most of the discussion hangs and from which the most important conclusions are drawn.

In industrial work, the purpose is essentially utilitarian, for the analysis is generally directed to finding the composition of commercial materials and to answering such questions as: (1) Does the material to be purchased correspond with the seller's description? (2) Is the material suitable for the purpose for which it is needed? (3) Is the material really worth the quoted price?

The Real Value of Rough Working Tests.—The practical potter usually tries how a small sample of the material to be purchased behaves in his oven and, if it satisfies that test, he accepts the bulk, believing with blind faith that all is right. It does not need the *subtilis diabolus*, referred to on page 110, to deceive him for, when it is worth while, it is comparatively easy to devise adulterations for most potter's materials which will make satisfactory trials. Although this simple test, invaluable in its way, may show (1) whether or not any *deleterious* impurity is present, or (2) whether the material is or is not capable of doing the work for which it is intended, yet (*a*) it gives no information as to the presence or absence of inert admixtures; otherwise expressed, it does not say whether the material offered for purchase really corresponds with the seller's description; and (*b*) it gives no idea whether the material is really worth the price asked.

Impurities in the Raw Materials.—An intimation to the vendor that the material may be tested is not sufficient security for the buyer. We are told that "of the samples of materials offered to a Government Department, approximately forty per cent. are either adulterated or of very inferior quality." Price is no criterion of the quality, for it is said that the most inferior samples were sometimes quoted at the highest prices. In such cases, analyses and

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[1] The work of C. F. Wenzel (1777) and of J. B. Richter (1791–1802) on chemical equivalents; the work of H. Cavendish (1784) on the composition of water; of C. W. Scheele (1779) on the composition of air; and the 1800–1808 controversy between C. L. Berthollet and J. L. Proust on chemical combination, illustrate the debt chemical theory owes to analytical practice.

[2] C. R. Fresenius, *Quantitative Chemical Analysis*, London, I, 4, 1876.

[3] H. S. Washington, *Prof. Paper U.S. Geol. Sur.*, 14, 13, 1903.

tests are the purchaser's only safeguard and the cost of the analysis in large deals may be recompensed a thousandfold.

Four samples of tin oxide from four different firms were submitted for analysis. The chemist reported that three of the samples were very nearly the same and contained approximately 99·5 per cent. of stannic oxide, but the fourth sample contained 5 per cent. of "combined water" and 0·05 per cent. of tungstic oxide as impurity. The potter's trials, however, showed that the cheapest and least pure sample gave the richest opaque glaze! The first three samples were approximately £228 per ton and the fourth sample £222 per ton. The potter subsequently obtained a rebate on account of the 5 per cent. of combined water, so that, while the effective tin oxide in the first three samples cost £229·15 per ton, in the fourth sample it cost £224 per ton. Incidentally he learned that he might be able to do with rather less stannic oxide than he had previously used when tin oxide was cheaper.

The Adulteration of Raw Materials.—So long as human nature is what it is, so long will adulteration be carried on with a view of making large profits and of cheating the purchaser into paying too high a price for his materials. *Caveat emptor*—let the buyer beware. A glance through the records of any testing laboratory shows that successful adulteration is one of the fine arts. Certificates of analysis of samples selected by the vendor are commonly presented as if some mysterious virtue resided in a material with such a certificate appended. The sample placed in the analyst's hands may or may not represent the material sold by the dealer. The onus of proof that the certificate really represents the materials received by the purchaser rests with the vendor (see page 110). The preceding example—tin oxide—was not a case of deliberate adulteration. The next case is not so clear.

A traveller offered a sample, A, of white lead at £28 per ton (5 per cent. moisture); another traveller offered another sample, B, at £25 per ton (5 per cent. moisture). The cheaper sample gave the better-looking frit when fused with a given proportion of ground flint in a biscuit cup in the usual way. Analysis showed that the cheaper sample B contained 69·0 per cent. of PbO and 15 per cent. of barium carbonate, whereas the dearer sample A contained 81·6 per cent. of PbO and no barium carbonate. Ground witherite (94–96 per cent. $BaCO_3$) was then worth about £10 per ton. The effective PbO in sample A would cost £34·31 per ton, and in sample B, £36·23 per ton. Hence, the dearer sample is the cheaper. The improved colour of the frit from the cheaper sample B was due to a known secondary effect of the barium salt which is of no significance when the material is used in bulk.

Standardising the Products of a Factory.—Analysis also furnishes a valuable means of keeping the finished products of a factory up to standard. Suppose that the body and glaze be analysed when everything is at its best, and the results be kept as standards. The standards are then very convenient for reference when substituting fresh clays or other raw materials, in order that the type of the new body may be kept as nearly as possible like the old one, thus lessening the risk of complications, *e.g.* with the glaze. In many cases, too, the cause of those perplexing faults which sometimes crop up, and which are usually attributed to the miller or to wrong mixtures, can be unerringly located and promptly rectified by a comparison of the analysis of the defective body or glaze with the standard.

A fresh batch of glaze turned out highly unsatisfactory. The glaze-mixer affirmed that he had mixed the glaze precisely as he had always done before and it was found that the defective glaze had received no different treatment from that regularly used on the works. The miller was accordingly blamed for the fault. He sent a sample of the defective glaze along with a sample of good glaze from the previous mixing for analysis. The analyst reported that the good glaze contained the equivalent of 24·5 per cent. of lead oxide, PbO, and the bad glaze but 5·5 per cent. The proportions of the other main constituents were the same in both glazes. The fault was obviously due

to a wrong mixing, in spite of affirmations to the contrary. When the proper proportion of white lead, computed from the analysis, was added to the defective glaze, it proved quite satisfactory.

The Imitation of Commercial Products.—In the *Sturm und Drang* of commercial warfare, it is not only necessary for a firm to test its own materials and products, but the "Intelligence Department" must also keep a watchful eye on the products of rival manufacturers.

A manufacturer has for years been supplying the trade with, say, an opaque glaze made from an old recipe—a legacy from the founder of the firm. For perhaps half a century there has been no change in quality for better or for worse, and the old recipe is the real master of the works. The traveller reports that he is seriously menaced by the success of a foreign glaze which is considerably better than his own and quite as cheap. Faith in the long-cherished recipe is shattered. After much worry and expense, trial and failure, the manufacturer is inclined to give up ignominiously beaten. As a last resource, he sends a sample of the foreign glaze to the expert analyst, requesting a recipe. The chemist recognises that it is not much use trying to reproduce the unknown glaze until he knows its composition. Guided by the analysis, it is comparatively easy to make a successful imitation of the competing glaze. There is no groping in the dark; success is not accidental and fortuitous, but the logical result of methodical work.

This may seem rather a low estimate of the function of an analyst, because a properly equipped staff would not be satisfied with its own old recipes. There would be no standing still. A firm would not wait until its position on the market was jeopardised or made untenable by a rival, but it would be continually experimenting not directly to imitate its competitors, but rather to beat its own products year by year.

Some Limitations of Analytical Chemistry.

How to Treat the Analyst.—Some have an extraordinary notion of the resources of analytical chemistry and inquiries are made for all manner of impossible things. A bottle containing about 100 c.c. of water was sent for analysis and the contents smelt strongly of a patent medicine! The subject of sampling is so important that a special chapter has been devoted to it—pages 110 to 122. When sending materials to the analyst, some consider it best to keep back information concerning the nature and origin of the sample so as to prevent a biassed report. The general effect of this procedure is to render the analyst's task more difficult and costly and to hamper his usefulness. Owing to the need for completing the analysis in a reasonable time and at a specified fee, an exhaustive search for every conceivable constituent is seldom made. An analyst working under normal conditions would certainly be excused if a clay with an abnormal amount of lithia were reported with soda in place of the lithia.[1] An example is indicated on page 123. This recalls the fact that

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[1] In this connection it is interesting to note that C. F. Plattner (*Pogg. Ann.*, 69, 443, 1846) was not able to make his analysis of the mineral pollux (from Elba) add up to 100 per cent., and he sought in vain for the missing element. After R. Bunsen and G. Kirchhoff (1860) had discovered cæsium, F. Pisiani (*Compt. rend.*, 58, 714, 1864) showed that Plattner had mistaken cæsium (atomic weight 132·9) for potassium (atomic weight 39·1). By making the corresponding correction, Plattner's analysis was found to be quite satisfactory. To make this quite clear, assume that 5 grams of a compound, supposed to be potassium chloride, are obtained. This will be multiplied by 0·632 to get the equivalent amount, 3·16 grams, of K_2O; but if the compound be CsCl, not KCl, then the weight must be multiplied by 0·837 to get the corresponding amount, 4·18 grams, of Cs_2O. The analysis would thus appear to be 4·18 less 3·16, that is 1·02 grams, too low if the 5 grams of cæsium chloride were mistaken for potassium chloride. This is a remarkable tribute to the accuracy of Plattner's analysis (J. W. Mellor, *Comprehensive Treatise on Inorganic and Physical Chemistry*, London, 2, 427, 1922). Lithium has a smaller atomic weight than sodium and accordingly, if much lithium is assumed to be sodium, the analysis will total too high.

the presence of arsenic in beer was not suspected until the 1900 epidemic of arsenical poisoning. Consequently, if the amount of any unusual constituent is desired, this should be specified.

The Fallibility of the Analyst.—Perhaps something of the feeling of awe and wonder which prevailed in the minds of the vulgar towards the alchemists of old survives to-day in the popular concept of the analytical chemist. Many apparently take it for granted that he is gifted with keener and more occult powers than his fellows. As a matter of fact, no one should be more conscious of his own limitations than the analyst himself, for he is continually humiliated and shamed by the fallibility of his own tests and by the resulting instability of his opinions. Analyses have been published which emphasise in a remarkable way how men exceptionally expert in one field of analysis fail ludicrously in an unfamiliar field. On one occasion, a report on china clay by an excellent county analyst "went the rounds." The report had a highly improbable number for the amount of alkali in the clay and stated that the alkalies were rather low, but the defect could be remedied by the addition of soda! In some cases, it is difficult to believe that the "reputed" analyses have been obtained other than by a process of guessing.[1]

Not infrequently a manufacturer has sent out samples to different chemists and had different results returned. He may have asked for explanations and decided in future to avoid the chemists as much as possible, concluding, as one expressed it, that "chemists are bluffers."[2] Unless two chemists are able to analyse the same sample with results acceptable to both buyer and seller, it is difficult to see what other conclusion the commercial man can draw. The utility of analyses in some of the industries has been discredited by ignorant, slovenly work which would be ludicrous were it not so pathetic. Faulty analyses have been discussed in several parts of this book[3]—*e.g.*, pages 214, 245, 387, 690, and 772. What H. S. Washington (1903)[4] has said of rock analyses in general applies even more emphatically to some published work on clays:

> There is a tendency to place implicit confidence in the results of analytical work—to accept readily whatever figures the analyst may furnish, with scarcely ever an attempt at a critical estimate of the worth of the analysis. It seems to be taken for granted that the analyst, like the proverbial king, can do no wrong. This applies not to the personal good faith of the analyst, but to the analytical processes which, possibly because they belong to one of the exact sciences, are for the most part tacitly assumed to be infallible. In few cases does there seem to be any recognition of the difficulties and uncertainties of analytical work.

The Fallibility of the Analysis.—Analytical operations are not performed with an automatic instrument which gives the composition of a substance with

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[1] J. Thoyst, *Des Fraudes dans les Essais contradictoires de Fer*, Paris, 1888.

[2] It was pointed out in *The Laboratory* (1, 334, 1867) that one source of the difficulty is due to the imperfect training of some who have started as professionals and who have to struggle for a living against competent men. By delivering lectures, judicious advertising, correspondence schools and book compiling on every possible occasion "Professor Saisrien" can depend on the public taking him at his word. He can "perform" analyses of every kind for a few shillings; the public blames chemists generally and the chemist gets all the discredit which may ensue when "Professor Saisrien" is employed.

[3] A discussion on the presence of titanic oxide in fireclays can be cited as an illustration of the value to be attached to some brick analyses, even by some who say they have analysed "hundreds of bricks," but who have apparently not troubled to find what methods are used by those who have specialised in producing accurate results.—A. R. Myhill, *Gas World*, 58, 299, 364, 1913; F. Harvey, *ib.*, 58, 323, 433, 1913; K. C. Orr, 58, 365, 1913; Anon., *ib.*, 58, 402, 1913.

[4] H. S. Washington, *Prof. Paper U.S. Geol. Sur.*, 14, 14, 1903.

machine-like precision. The presence or absence of each constituent has to be established by special tests and the amount determined by a number of operations, each of which introduces a small error into the final result. The limits of error in the more frequently conducted operations are fairly well known and, to those familiar with that type of work, the precautions needed to reduce the errors to a minimum are a part of their routine practice. With those substances which are not analysed so frequently, the errors are probably somewhat greater, for the disturbing factors are not so well known. At best, however, few analytical operations are altogether free from error and vexation of spirit, and the work is done more or less blindly, quite in ignorance of the why and the wherefore.

Standard Methods of Analysis.—When different chemists present conflicting results, discord is sure to arise in settlements between buyers and sellers and in the control of works processes. As a result, many corporate bodies have been driven to insist on the use of certain uniform methods of analysis in testing the materials in which they are interested. The idea has been taken up seriously by a number of chemical societies, and there is now quite a number of so-called "Official or Standard Methods of Analysis" for particular substances—*e.g.* fertilisers and food-stuffs (*vide* page 246). The idea is to secure concordant analyses, to reduce errors to a minimum and to place commercial analytical practice on a higher plane. The proposed methods are not fixed for all time, but are revised periodically so as to substitute improved methods when such are available.

Standardised Samples.—In 1905, the American Foundryman's Association prepared with great care a set of samples of iron, had them analysed by three or four chemists of recognised ability and sold portions as "standardised samples" at a reasonable price. The idea has since been further elaborated by the Bureau of Standards, Washington, U.S.A., and other bodies from which "standardised samples" with detailed certificates of analysis can be obtained. The work has up to the present been largely restricted to alloys and ores of various kinds.[1] Some of the uses of standardised samples are as follows:

(1) An analyst unfamiliar with a particular analytical process can practise with the analysed samples until he is perfected. The standardised samples also furnish useful checks for advanced students of quantitative analysis.

(2) The applicability and accuracy of a new or "improved" method of analysis can be determined with comparatively little effort by working with standardised samples.

(3) In cases of disputed results, owing to the use of faulty methods of analysis by one of the chemists, both parties can analyse a standardised sample and find who is at fault before the case comes into court. This seems more satisfactory than submitting the original sample to a third party as umpire, because the umpire may be no more capable than the contending analysts.

The Evolution of Modern Analytical Practice.

How Analytical Processes have Grown.—A comparison of the classical textbooks of H. Rose (1829), C. F. Rammelsberg (1845), C. R. Fresenius (1841-6), C. F. Mohr (1855), and L. E. Rivot (1861-6) with those published in more recent years shows that the development of the art has been painfully slow. Many, perhaps most, of the standard processes are purely empirical or rule-of-thumb. The original methods devised by the fathers of analytical chemistry gave more or less approximate results; with increasing experience, these processes were modified—now here, now there—until methods were evolved

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[1] *U.S. Bur. Standards Circulars,* Nos. **25, 26** and **40**; W. F. Hillebrand, *Journ. Ind. Eng. Chem.,* **1**, 41, 1909; W. C. Ebaugh, *ib.,* **1**, 63, 1909; L. C. Jones, *ib.,* **1**, 269, 1909; W. D. Richardson, *ib.,* **1**, 5, 1909.

which would furnish results accurate within the limits of experimental error tolerated in practice.   No entirely satisfactory method has as yet been evolved for the complete analysis of a mixture of the rare earths; while the elaboration of the regular methods for the determination of phosphorus, magnesia, sulphur and potassium, the chromate process for the separation of barium and strontium, the sulphide processes for the separation of antimony and tin, and for the separation of zinc, and the well-known basic acetate process, all bear eloquent testimony to the adventitious and empirical way the art has developed.   Much work has been directed to developing speed without sacrificing accuracy, and towards determining one or two constituents in a mixture and ignoring the others.   Hence, some industrial routine processes have been abridged (mechanicalised) into a rigid code of instructions such that boys or girls—"testers," as they are called—of no special education or preparation, can be taught in a short time to perform the necessary operations and get good results.

The Substitution of New Processes.—Owing to the curious evolution of the processes used in analytical chemistry, analysts are reasonably reluctant in introducing new methods.   It is not wise to substitute comparatively untried processes—however promising they may appear—without very careful consideration.   The dread of incorporating unknown errors in our work begets caution,

> And makes us rather bear those ills we have
> Than fly to others that we know not of.

In an old, long-tried process, the disturbing factors and the precautions necessary for accurate work are fairly well known, whereas with a novel process much has to be learned in humouring its little idiosyncrasies in order that it may give the best results.   In spite of this conservatism, a number of new processes have been introduced in recent years and many of them have won, or are winning, their way into general practice.   A noticeable feature of modern analytical work is the increasing use which is being made of organic reagents such as a-nitroso-β-naphthol, dimethylglyoxime, a-benzoin oxime, "cupferron," 8-hydroxyquinoline, diphenylcarbazide and thioglycollic acid.[1] Many separations can be expedited by some of the newer methods, which are accordingly often recommended in preference to the older processes.

The Variety and Diversity of the Work in the Silicate Industries.—The methods of analysis for clays and related silicates are fairly general and need little or no modification from sample to sample; it has therefore been possible to give a detailed scheme for their analysis in Part II, and this is used as a standard of reference for the remainder of the book.   The case is very different with glazes and enamels, for it is not often that two consecutive analyses can be conducted by exactly the same method; the change in method from sample to sample is still more pronounced in dealing with colours.   Some of the materials submitted for analysis involve extremely difficult separations and a special method must be devised to suit each case.   Sometimes, too, the report of the analysis has to be accompanied by a working recipe and, with the more delicate colours, this is a severe test of the accuracy of the work.   One month, for example, an enamel containing arsenic, antimony, tin and fluorine was followed by a black colour containing iron, chromium, manganese, cobalt and zinc; and this, in turn, by a pink colour containing gold, silver, tin and lead.   In

[1] H. Grisollet and M. Servigne, *Ann. Chim. anal. Chim. appl.*, **12**, 321, 1930; J. Grant, *Ind. Chem.*, **7**, 197, 227, 1931; Hopkins and Williams, *Organic Reagents for Metals*, London, 1934; F. Feigl, *Ind. Eng. Chem. Anal. Ed.*, **8**, 401, 1936.

each case, these elements were accompanied by the ubiquitous silica, alumina, alkalies and alkaline earths and, in three cases, by boric oxide. There was also an inquiry for an examination of a faulty oleaginous platinum lustre for elements of the platinum group other than platinum.

Unfamiliar Operations.—Although the proportion of analyses of complex mixtures of the kind just indicated to analyses of clays, bricks and related materials, which are required from a ceramic-testing laboratory, is relatively low, yet it would be a mistake to cut down the directions for the analysis of the less frequently occurring substances because of their rarity. On the contrary, fuller minutiæ are then required because, the less familiar the road, the greater the need for guide-posts and danger signals and the greater the probability of "accidental errors." So many cases have arisen where schemes for the analysis of unfamiliar mixtures are not included among those given as types in text-books on quantitative analysis, that much time must have been wasted in devising feasible processes, even when a good library was available. It is quite impracticable to describe methods suited to every possible or likely case which might be required in practice; nor did it seem to us so expedient to give detailed schemes for a few mixtures as to take an imaginary mixture, more complex than would obtain in practice, and indicate the short-cuts to be made when the qualitative analysis shows that the conditions are favourable. It is thus nearly always possible to curtail the general schemes—pages 327, 413, 572—to suit particular cases, of course bearing in mind the hints given on page 277.

The Theory of Analytical Operations.—The technique of analytical chemistry has been worked out without much aid from theory, for the classical text-books have merely elaborated details of manipulation necessary for exact results. In 1894, W. Ostwald demonstrated the important bearing which the theories of physical chemistry have upon the practice of analytical chemistry. Opinions may differ very much as to the function of the *ionic hypothesis* in analytical chemistry,[1] and whether anything is really gained by describing the facts of an essentially practical art in the language of a very hypothetical doctrine. Excluding this hypothesis, perhaps the most important ideas derived from physical chemistry which have tempered analytical operations are: (1) The theory of *adsorption* (pages 86, 160, 691, etc.). It seems to be impossible to wash a precipitate perfectly free from adsorbed liquids or solids, although it is usually possible to make the error so introduced negligibly small. (2) The laws of *the colloidal state of matter* (pages 84, 152, 274, etc.). When an "insoluble" precipitate separates from a solution in the absence of dissolved electrolytes, it is frequently in the colloidal condition, and it cannot then be isolated by filtration and washing. An electrolyte must be added in order to get the substance in a condition suited for treatment. (3) The theory of *incomplete reactions* (pages 162, 271, etc.). The reactions which result in precipitation and neutralisation are not usually complete. Instead of running to an end, the system takes up a state of equilibrium between the initial (or solution) stage and the final (or precipitate) stage, and a certain amount of the element under investigation escapes precipitation. Perfect separations by precipitation are not therefore possible and consequently it is desirable to study each process with the object of finding the conditions necessary to make the precipitation complete enough for practical requirements.[2] This is partly what is meant by "humouring an analytical process."

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[1] According to O. Hackl (*Jahrb. K. K. Geol. Reichsanstalt,* **62**, 613, 1913), the application of the ionic theory in analytical chemistry has been of no practical or theoretical advantage!

[2] See L. Moser, *Zeit. anal. Chem.,* **59**, 1, 1920.

PART I.
GENERAL.

CHAPTER I.

WEIGHING.

§ 1. The Balance.

Weighing is, no doubt, a mechanical operation, but yet is of singular service not only in investigating the properties of bodies but in directing those properties to their proper uses.—T. BERGMAN.

THE balance is one of the most important instruments used by the analytical chemist. It is essentially an instrument for comparing weights. The object of weighing is to compare the quantity of matter in a given substance with the quantity of matter in a standard substance—the weight or weights.[1] The conditions which must be satisfied by a good balance are:—

(1) The balance must be consistent. It must give the same result in successive weighings of the same body. This condition depends upon the accuracy of the knife-edges.

(2) The balance must be accurate. The beam must be horizontal when the pans are empty and when equal masses are placed on the pans. This condition depends upon the equality of the two arms. To eliminate any error arising from the inequality of the arms of the beam see page 14.

(3) The balance must be stable. The beam after being displaced from its horizontal position must return to its horizontal position. This condition depends on the adjustment of the centre of gravity.

(4) The balance must be sensitive. It must show any inequality in the two masses on the scale pans even when the differences are small.

(5) The balance beam must oscillate quickly. The time taken for an oscillation of the beam, as indicated by the pointer, should be as small as possible, in order that the weighing may be done quickly.[2]

§ 2. The Location, Care and Use of the Balance.

If the balance be in danger of vibrations, shocks or jars while in use, it should be placed on a firm foundation—either on solid masonry built from the ground, or isolated from the floor vibrations by resting it on a shelf fixed to heavy brackets against the walls, and not with legs resting on the floor. The balance should be adjusted perfectly horizontal by means of the levelling screws and the spirit level or plumb bob inside the case.

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[1] The theory of the balance is usually discussed in text-books on physics. The student is referred to J. Walker, *The Theory and Use of a Physical Balance*, Oxford, 1887; E. Brauer, *The Construction of the Balance*, London, 1909; W. S. Aldis, *Trans. Newcastle Chem. Soc.*, 3, 151, 161, 1876; P. J. Krayer, *The Use and Care of a Balance*, Easton, Pa., 1913; F. A. Gould in R. T. Glazebrook's *Dictionary of Applied Physics*, London, 3, 107, 1923.

[2] For the limitations of the balance, see B. Blount, *Journ. Chem. Soc.*, iii, 1035, 1917.

The balance should be located so that it is not likely to be heated unequally,[1] and therefore it should not be placed near a door frequently opened, nor adjacent to a stove, hot-water pipe, window or ventilating shaft. If the location be not suitable, the "zero point" of the balance will be continually changing owing to the unequal expansion of the arms. If possible, the balance should be kept in a separate room. If a small room cannot be partitioned off from the laboratory, a second glass case covering the balance case proper may be needed. Keep the mechanism free from dust. Hence, the balance case must not be opened in a dusty room. If artificial light be used, it should be above and at the back—if possible, over the right shoulder—of the operator.

If there be any likelihood of the atmosphere in the vicinity of the balance being contaminated with acid fumes, lime and alkaline carbonates should be kept in the balance case to neutralise their effects. Calcium chloride is frequently kept inside the balance case in glass vessels made for the purpose, or in a funnel, which in turn rests in an Erlenmeyer's flask. The idea is to keep the atmosphere inside the case dry. The remedy is by no means effective, as will be shown later. A mixture of fragments of quicklime and granulated calcium chloride is good. Some object to the use of concentrated sulphuric acid as a desiccating agent in the balance case owing to the fumes (sulphur dioxide) which are given off when organic dust collects in the acid jar.[2]

The object to be weighed should neither be (1) hotter, nor (2) colder than the atmosphere in the balance case. Currents of hot air may impinge on the arms of the balance and cause one arm to expand unequally, or buoy up the beam. For instance, a platinum crucible which appeared to weigh 20·649 grms. when warm, really weighed 20·692 grms. when cold. Hence, the crucible weighed 0·2 per cent. less when hot than cold. If the crucible be colder than the atmosphere of the balance case, moisture may condense on the object to be weighed. If the object to be weighed is likely to be electrified, it should be allowed to stand some time after it has been wiped, before it is weighed.[3] The electrification of the weights [4] or objects causes erratic movements of the pointer.

The balance should not be cleaned too frequently. With proper care and the balance in a suitable position, a good cleaning every three or four months should suffice. This may occupy from a quarter to an hour. All the loose parts should be carefully removed and dusted; the movable parts cleaned and oiled. Wipe off any excess of oil. Polish the suspensions with a piece of chamois leather. Restore all the parts. Adjust the equilibrium screws and gravity bob as indicated later in this chapter. The weights can be tested at the same time.

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[1] If one arm be 1° hotter than the other, the error introduced in a weighing amounts to about 0·001 grm. on a 50-grm. load, and proportionally less for a smaller load. W. H. Miller (*Phil. Trans.*, 146, 753, 1856) detected a difference of 0·00001 mm. in the thermal expansion of the two arms arising from a change in the temperature of the room. The arms expanded unequally owing to a difference in the quality of the metal forming the beam. T. Middel, *Drude's Ann.*, 2, 115, 1900; P. Schwirkus, *Zeit. Instr.*, 7, 42, 1887; J. J. Manley, *Trans. Roy. Soc.*, A, 210, 387, 1910.

[2] G. S. Johnson, *Chem. News*, 67, 211, 1893. Compare J. J. Manley, *Phil. Mag.*, (7), 16, 489, 1933.

[3] J. A. R. Newlands, *Chem. News*, 11, 107, 1865.

[4] Quartz weights (H. Buff, *Dingler's Journ.*, 222, 159, 1878; S. Stein, *Zeit. anal. Chem.*, 17, 471, 1878; glass weights—R. Ulbricht, *Ber.*, 10, 129, 1877) in a velvet-lined box are liable to become electrified as they are removed from their bed (*Chem. Ztg.*, 12, 494, 1888). See page 622. R. Hennig (*Zeit. Instr.*, 5, 161, 1886) discusses the errors due to air currents which are set up when liquids are weighed in open vessels.

§ 3. Weighing Hygroscopic or Volatile Liquids and Powders.

Small crucibles, watch-glasses, basins, capsules or glazed paper,[1] are convenient supports for substances not affected by exposure to the air while being weighed. Hygroscopic, efflorescent and volatile substances, and substances liable to absorb carbon dioxide from the air must, if possible, be weighed in closed vessels or clipped watch-glasses with ground edges. A selection of such vessels is shown in fig. 1. The weighing bottle or tube must be adapted for the material under investigation. Weighing tubes must be suitably supported. The stand shown in fig. 1a is suitable for supporting a
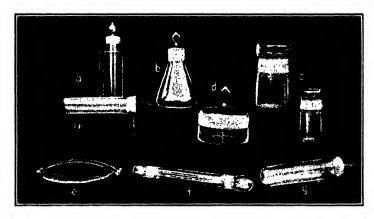
Fig. 1.—Weighing Bottles and Weighing Tubes.

tube either vertically or horizontally. The weighing tube may be permanently closed at one end and fitted with a ground stopper or cap at the other—fig. 1a; or it may have a ground cap at both ends—fig. 1f. Weighing tubes for boats may have two legs to prevent rolling—fig. 1g.[2] Watch-glasses with ground close-fitting edges are clamped together by a suitable clip as shown in fig. 1e.[3] Weighing bottles may have different shapes and sizes—figs. 1b, 1c, 1d. Guttmann's weighing bottles, fig. 1c, with ground caps, are best for weighing out powders by difference,[4] since (1) several portions can be weighed out successively without the joint having to be cleaned, as is necessary with the ordinary ground stopper, and (2) dust does not accumulate between the stopper and the ground surfaces. A modification with ground-in tubes is useful for drying substances in a current of gas, for determining water of crystallisation, etc.—fig. 137.

The capped weighing bottle may also be used for weighing liquids—fig. 2. The tube with the liquid has a small pipette inside. All is weighed. Some

[1] Paper, horn capsules and similar substances are somewhat hygroscopic and vary in weight with the humidity of the air. "Xylonite paper" has many advantages over ordinary glazed paper. It is less hygroscopic; it can be washed with water; it is not attacked by ordinary acids and alkalies. It is attacked by organic solvents (H. Schweitzer, *Chem. Ztg.*, **14**, 698, 1890). H. F. von Jüptner, *Die Einführen einheitlicher Analysenmethoden*, Stuttgart, 261, 1896.

[2] A. Gawalovski, *Chem. Centr.*, (3), **16**, 369, 1886.

[3] J. J. Griffin, *Chem. News*, **101**, 71, 1910; K. Buschmann, *Chem. Ztg.*, **30**, 1060, 1906; F. Hall, *Journ. Amer. Chem. Soc.*, **37**, 2046, 1915; G. Incze, *Zeit. anal. Chem.*, **54**, 406, 1915.

[4] C. Mangold, *Zeit. angew. Chem.*, **4**, 441, 1891; L. F. Guttmann, *Journ. Amer. Chem. Soc.*, **28**, 1667, 1906; A. Breneman, *Chem. News*, **48**, 168, 1883; T. Zöhren, *Chem. Ztg.*, **36**, 824, 1912; F. Friedrichs, *Zeit. anal. Chem.*, **53**, 177, 1914.

liquid is withdrawn by means of the pipette.[1] The pipette is returned to the bottle, and all is weighed again. The loss in weight represents the amount of liquid removed. Berl [2] has a convenient pipette for weighing corrosive liquids —fig. 3. The apparatus is weighed. The tap C fits closely without lubrication. To fill the pipette, connect A with K; apply suction at A, until K is partially evacuated, then close C. Let the point S dip in the liquid under examination; connect P and K. The liquid runs into the pipette. Close the tap C before the liquid has reached it. Clean the end of the tube S. Return the pipette to the tube F and weigh. The increase in weight represents the amount of liquid in the pipette. Now let the tip S dip under water. Let the contents gradually run from the pipette by opening the cocks. Run water through the apparatus. This will ensure the removal of all the liquid from the pipette.[3] This procedure may be obviously modified to suit particular conditions.[4] The instrument is rather lighter than Lunge and Rey's well-known pipette for a similar purpose.

Large glass and porcelain vessels, platinum crucibles and basins dried and cooled in desiccators, are particularly liable to condense moisture on their surface while being weighed.[5] Many powdered substances also begin to absorb moisture and possibly also other gases quite energetically immediately they have left the desiccator, and Pagasogli [6] mentions an example where a powder dried over sulphuric acid increased in weight from 0·001 to 0·003 grm. during the weighing, which occupied between 3 and 6 minutes. The weight of a body will increase until the vapour pressure of the absorbed moisture is equal to the vapour pressure of the moisture of the air. The practice of keeping a desiccating agent in the balance case with the idea of retarding the absorption of moisture while the substance is being weighed is not particularly efficacious.

FIG. 2.—Weighing Bottle and Pipette.   FIG. 3.—Berl's Weighing Pipette.

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[1] For a weighing bottle with a pipette stopper, see L. E. Levi, *Journ. Amer. Chem. Soc.*, 27, 614, 1905.

[2] E. Berl, *Chem. Ztg.*, 34, 428, 1910; H. Rosenlecher, *Zeit. anal. Chem.*, 37, 209, 1898; G. Lunge and H. Rey, *Zeit. angew. Chem.*, 4, 702, 1891.

[3] For strong fuming acids, a drop of liquid may escape from S into the tube F while it is being weighed. In that case, a drop of water is placed in F, and all is weighed without allowing the tip of the tube S to be wetted. The pipette is then filled as described in the text. Berl has modified the bulb for liquids with a high vapour tension (*i.e.* volatile liquids).

[4] When weighing liquids which spoil on exposure to the air, Holde's pipette may be used. D. Holde, *Zeit. angew. Chem.*, 12, 711, 1899; H. Schweitzer, *Journ. Amer. Chem. Soc.*, 15, 190, 1893; E. Reichardt, *Zeit. anal. Chem.*, 7, 187, 1868.

[5] Vessels full of air have a uniform weight as soon as their surfaces are in equilibrium with the atmosphere. When these conditions are changed—by a variation of temperature for example—it takes a long time to bring the vessels to their original condition. Thus, a hard glass tube, 60–80 cm. long and 2–2·5 cm. diameter, must be kept two or three hours in a balance case before its weight is constant. Glass flasks, 1 to 4 litres capacity, after having been heated or rubbed, do not attain a constant weight until they have remained in the balance case five or six hours. Polished platinum rapidly regains its primitive weight, but when the surface is more or less roughened, it attains its proper weight more slowly than glass or porcelain. J. S. Stas, *Œuvres Complètes*, Bruxelles, 1, 317, 1894; *Chem. News*, 4, 206, 1861; J. L. Smith, *ib.*, 31, 55, 1875.

[6] G. Pagasogli, *L'Orosi*, 10, 109, 1888; J. L. Smith, *Chem. News*, 31, 55, 1875. Compare J. Rehner, junr., *Zeit. anal. Chem.*, 88, 266, 1932.

This is well illustrated by the following observations:[1]—A hair hygrometer was placed in a balance case. Some fresh granulated calcium chloride was placed in a funnel resting over a flask. The hygrometer showed a humidity of 60·5 to 61 per cent. In an hour, the humidity fell to 55·5 per cent.; in 15 hours, to 53·5 per cent. The humidity then gradually rose during the next three days to its former value, 60–61 per cent. The calcium chloride was then appreciably moist and liquid began to drop from the end of the funnel.

Ostwald[2] recommends weighing the substance as rapidly as possible after removing the vessel from the desiccator. The idea is to make the error due to adsorption as small as possible. In igniting or drying to a constant weight, the same time may not always be occupied in making the control weighings and different results may accordingly be obtained with the same body. For instance, three control weighings of the same body gave 17·4334, 17·4332, and 17·4331. The idea is best applied by getting the approximate weight of the ignited body in a covered crucible. Repeat the ignition and cooling, and place the necessary weights on the pan, so that the rider alone is needed to complete the weighing. This will usually suffice, but a third ignition will enable the third weighing to be made in a few seconds.

On the other hand, Smith[3] recommends leaving the body 20 minutes in the balance case after it has been removed from the desiccator, in order that the body may adsorb its normal film of moisture, i.e. until its weight is constant. The objection to this plan is the long time required for the control weighings, and there is nothing to show that the humidity of the atmosphere has remained constant during the experiment. However, it is not likely to change appreciably under ordinary conditions.[4]

§ 4. Some Points on Weighing.

In attempting to weigh to the tenth of a milligram, it might be thought best, at first sight, to add weights and move the rider until the pointer of the balance swings equally on both sides of the zero of the scale. It is assumed, quite correctly, that when the exact weight has been added to a properly adjusted balance, the pointer will swing the same number of divisions to the right and the left of the zero, provided it does so when the pans are empty. As a matter of fact, this method is perhaps more often in error than otherwise. It entails a frequent adjustment of the zero point of the balance, owing to unavoidable variations in the zero point.[5] Even if the position of equilibrium of the pointer with an unloaded balance be adjusted with the pointer at the zero of the scale, the zero point may change in a short time, owing to unequal heating of the arms, and other causes. By ignoring this fact, appreciable errors may creep into the work. This method of weighing, in which the rider is adjusted until the swing of the pointer of the loaded balance is nearly the same as with the unloaded balance, is very common, and it is accurate enough

[1] O. Kuhn, *Chem. Ztg.*, **34**, 1097, 1108, 1910.
[2] W. Ostwald and R. Luther, *Hand- und Hülfsbuch zur Ausführung physiko-chemischer Messungen*, Leipzig, 51, 1902; London, 38, 1899.
[3] J. L. Smith, *Amer. Chemist*, **5**, 212, 1874; F. P. Treadwell, *Kurzes Lehrbuch der analytische Chemie*, Leipzig, **2**, 21, 1911; New York, 22, 1904.
[4] R. Hottinger (*Zeit. anal. Chem.*, **48**, 73, 1909) recommends plotting the increases in weight as ordinates, with time as abscissæ. The curve will be horizontal after the elapse of a few minutes. The first weighing will not be zero. The time required for the first weighing is longest; subsequent weighings occupy less time. Hottinger extrapolates for zero by continuing the curve. F. Richarz, *Verhandl. phys. Ges. Berlin*, 83, 1886.
[5] T. E. Thorpe, *Journ. Chem. Soc.*, **47**, 116, 1885; J. J. Manley, *Proc. Roy. Soc.*, A, **86**, 591, 1912; *Trans. Roy. Soc.*, A, **212**, 227, 1912.

for most analytical work. We shall see later that the errors incidental to the methods of preparing precipitates for weighing, mask the small errors introduced by the effects just indicated.

In special cases, when weighing to the tenth of a milligram, it is important to be able to make the weighing independent of any temporary inequality of the arms, etc. Hence we have:—

(1) *Gauss' method of double weighing.*—The object is weighed first in one pan, then in the other. The square root of the product is supposed to represent the weight of the object.[1]

(2) *Borda's method of weighing by tares.*—Here the object is balanced by a suitable tare (wire, weights, shot, potash bulb, etc.). The object is removed, and weights are added in its place until equilibrium is restored.

(3) *Method of weighing by double vibrations (or swings).*[2]— The following description may make the process of weighing by double vibrations appear somewhat laborious. The labour is, however, more apparent than real. Practice with the method is also an excellent way of mastering the manipulation of the balance.

First, find the zero position of the pointer, that is, the position the pointer will occupy on the scale when the balance, swinging without a load, comes to rest.
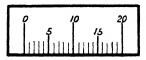
Fig. 4.—Scale of Pointer of Balance.

It would be too great a waste of time to wait until the oscillations of the pointer cease when it is possible to deduce the position directly from the distances the pointer swings to the left and right of the scale. Following F. Kohlrausch,[4] we prefer to number the scale with the zero on the extreme left, not in the middle of the scale. This prevents any confusion of signs later on. Neglect the first two or three swings on account of the shock and air currents set up when the door of the balance is closed. Take 3, 5 or 7 consecutive readings of the turning points of the swinging pointer. Take the average of the odd and also the average of the even numbered readings. Add the two results and divide by 2. In illustration, suppose the turning points read—

$$7 \cdot 2; \quad 13 \cdot 0; \quad 7 \cdot 2$$

The mean of the first and third readings is 7·2; the mean of both the even and odd readings is 7·2 + 13·0 divided by 2, that is, 10·1. This number represents the required zero point of the balance. The needle will come to rest when the pointer is at 10·1.[5]

Second, find the deviation of the scale per milligram, that is, the sensibility of the balance. The object to be weighed is placed on the left pan, the weights on the right pan. When the weights [6] are so far adjusted that another centigram

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[1] *Chem. News*, **106**, 248, 259, 1912. For an extension of Gauss' method, see A. E. Conrady, *Proc. Roy. Soc.*, A, **101**, 211, 1922; W. H. J. Vernon, *Journ. Soc. Chem. Ind.*, **53**, 211, 1934.

[2] For details see text-books on physics. J. H. Poynting, *Chem. News*, **39**, 45, 1879; *Proc. Manchester Lit. Phil. Soc.*, **18**, 33, 1879.

[3] The reading of the pointer in accurate work is greatly facilitated by the use of a lens or a magnifying mirror made for the purpose. The lens or mirror is so arranged that an enlarged image of the pointer and scale meets the eye when the head is in its natural position before the balance.

[4] F. Kohlrausch, *Leitfaden der praktischen Physik*, Leipzig, 44, 1896.

[5] Scales with red lines instead of the black ones are claimed by C. M. Clark (*Journ. Amer. Chem. Soc.*, **32**, 884, 1910) to be more easily read.

[6] For the condensation of "moist air" on the weights, see T. Jhmori (*Wied. Ann.*, **31**, 1006, 1887) and E. Warburg (*ib.*, **27**, 481, 1886). H. V. Moyer and P. K. Winter (*Ind. Eng. Chem.*, **26**, 238, 1934) recommend chromium-plated weights.

weight would be too much, close the door of the balance case, and move the centigram rider on the divided beam until the pointer moves to the right and left of the 10th division. Find the position of rest, e.g.—

Weight on Pan.	Turning Points.	Averages.	Zero Point.
11·216	8·2; 13·3; 8·4	8·3; 13·3	10·8

Move the rider another milligram division to the right.

Weight on Pan.	Turning Points.	Averages.	Zero Point.
11·217	4·1; 11·6; 4·3	4·2; 11·6	7·9

Hence, the zero point is displaced $10·8 - 7·9 = 2·9$ divisions by increasing the weight 1 milligram; or 2·9 scale divisions correspond with 1 milligram. This number, 2·9, represents the required sensibility of the balance for the given load. The sensibility of a balance for a given load is therefore defined as the displacement of the position of rest of the beam produced by an excess of 1 milligram weight on either pan.

Third, calculate the weight of the load on the pan. From the preceding results, it follows that the load weighs $11·216 + x$ grms. The zero point of this load is displaced $10·8 - 10·1 = 0·7$ scale division. Since 2·9 scale divisions correspond with 1 milligram, 0·7 scale division will correspond with $0·7 \div 2·9 = 0·24$ mgrm. Hence the weight of the body is $11·216 + 0·00024 = 11·21624$ grms. These calculations may be summarised in the formula

$$\text{Correction} = +\frac{a - z}{a - b}\text{mgrm.}$$

where z represents the zero point of the unloaded balance; a, the zero point with not quite sufficient weight on the right pan; and b, the zero point with a milligram more on the right pan than corresponds with a.

The ordinary analytical balance does not indicate with certainty smaller weights than 0·0001 grm. Hence, although the weight has been stated to the fifth decimal, in future weights will generally be rounded off by dropping the fifth decimal and raising the fourth decimal one unit when the dropped figure exceeds 5. It is well to keep rigidly to one routine process, so that the preceding operations may become mechanical. With a little practice, time is saved owing to the fact that no useless trials are made in the final adjustment of the rider. The result is also more exact than the method of weighing by equal deviations of the zero point.

§ 5. The Sensibility of the Balance.

Balances may now be obtained which show practically no change in sensitiveness $(a - b)$ between full and empty loads. The mere statement that "a balance is sensitive to $\frac{1}{10}$th mgrm." is not sufficient unless the corresponding load be specified. A balance carrying 5 grms. might be sensitive to $\frac{1}{10}$th mgrm., whereas $\frac{1}{10}$th mgrm. with a load of 100 grms. would have no perceptible influence on the movements of the beam.

Most balances have a "gravity bob" screw attached to the central portion of the beam, or a sliding weight on the pointer. The gravity bob provides a means of regulating the value of $(a - b)$, the sensitiveness of the balance, within certain limits.[1] By its means, the distance between the centre of gravity and the central knife-edge can be altered; and the nearer the centre of gravity to the central knife-edge, the greater the sensibility and the greater the period

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[1] For a device for adjusting the centre of gravity, see C. Bunge, *Chem. Ztg.*, **37**, 280, 1913.

of vibration of the balance. If the gravity bob be too near the central knife-edge, the time of vibration is too long and the balance will be too sensitive; if the gravity bob be too far away from the central knife-edge, the balance may be unstable, either with the empty pans or with a full load. It is generally possible, by adjusting the gravity bob, to make the numerical value $(a - b)$ a single figure. Suppose, for example, we have a balance of constant sensibility so adjusted that its sensibility is 0·7, the work of weighing is much simplified. For instance, in weighing a platinum crucible, we simply find—

	Turning Points.	Zero Points.
Unloaded	5·4; 17·6; 5·6	$z = 11·55$
Loaded 20·023 grms. . . .	6·0; 18·7; 6·2	$a = 12·40$
Displacement of zero point . . .		$a - z = 0·85$

Hence, $0·85 \div 0·7 = 1·2$. The required weight is 20·0242 grms. With such a balance, properly adjusted, a weighing is very quickly and accurately performed.

If the sensibility of the balance varies a little with the load,[1] as is usual with common analytical balances, owing to a slight bending of the loaded beam,
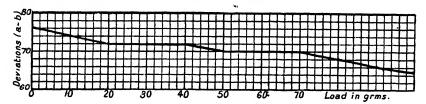
FIG. 5.—Variation of Sensibility of a Balance with Load.

it is simplest to determine the value of this constant for the different loads once for all. Suppose we find for a certain balance—

Load . . 0, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 grms.
Deflection . 0·76, 0·74, 0·72, 0·72, 0·72, 0·70, 0·70; 0·70, 0·68, 0·66, 0·65 divs.

The value of $a - b$ can then be read at a glance, for any given load, from the graph of these numbers (fig. 5). When $a - b$ is so fixed, a and z are alone determined each weighing.

§ 6. The Accuracy of the Weighing.

The finest weighing cannot compensate for the lack of purity of substance, or the absence of perfection in chemical operations.—G. D. HINRICHS.

Accurate measurement is the foundation of real science, and it is necessary to get clear ideas about the principles of measurement in analytical chemistry. It would obviously be an absurd waste of time to weigh to an accuracy of 0·001 per cent. at one stage of the work, if at another stage of the work the method of preparing the substance for weighing introduced an error of 0·5 per cent.

Although many errors are small enough to be neglected, yet cases often arise where errors, trivial under one set of conditions, assume serious dimensions under another set. Hence, it is necessary for every analyst to have clear ideas of the character of the different errors which may affect his work, in order that

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[1] H. R. Proctor, *Chem. News*, 30, 255, 1874.

corrections may be introduced whenever necessary. A chemist will not consider any time lost which is necessary for obtaining accurate results; but it is certainly a waste of time to carry the accuracy of any single operation (*e.g.* weighing) much beyond the limits of experimental error incidental to the process of analysis.

Errors in weighing and measuring should fall well within the limits of the experimental error due to the analytical operations. There is no advantage in making one of a series of interdependent measurements much more accurate than the others. A chain is no stronger than its weakest link. Under ordinary conditions, ten consecutive weighings of the same substance should not differ much more than 0·0005 grm., that is, by 0·05 per cent. working with one-gram samples; whereas in other cases the error in weighing should not exceed 0·01 per cent., that is, 0·0001 grm.

EXAMPLE.—If an error no greater than 0·001 grm. were made in the initial weighing of a gram of a clay which contained 0·2 per cent. of MgO, the greatest error in the determination of the magnesia could be no greater than 0·1 per cent. of its value. That is, the final result could not be affected by more than 0·1 per cent. of 0·2 per cent., *i.e.* 0·0002 grm. This is negligibly small. The weighing is even more accurate than is necessary. Suppose further that an error of 0·001 be possible in the weighing of the 0·0055 grm. of $Mg_2P_2O_7$;[1] an error of 0·001 grm. would represent an error of $100 \times 0·001 \div 0·0055 = 18$ per cent. This is too great. The weighing must be more exact.

Clay analyses are usually made upon one-gram samples. The final result is represented as a percentage taken to the second decimal. This seems to imply that the weighings are exact to the 0·0001th of a gram. Possibly they are. It would not be very difficult to make the weighings exact to 0·00001th grm. This would enable us to represent the final analysis, as beginners frequently do, with three decimals. But we shall see that the appearance of accuracy conveyed by these decimal figures—the second and third—is quite illusory.[2] *Calculations should stop when the limit of precision of the analytical process is reached. Precision in form does not necessarily represent accurate work.*

Altogether apart from the accuracy of the sampling, analytical operations involved in preparing the different substances for weighing are seldom more exact than is represented by Washington's[3] statement: "For silica or other constituents which amount to 30 per cent. or over, the allowable limits of error are 0·2 to 0·3 per cent. of the whole material; for alumina and other constituents which amount to from 10 to 30 per cent., 0·1 to 0·2 per cent.; and for constituents which amount to 1 to 10 per cent., 0·05 to 0·1 per cent." If we accept these numbers as representing the errors incidental to the best processes available for the analysis of silicates and clays, it will be obvious that little, if anything, is gained by increasing the accuracy of the weighings beyond the tenth of a milligram, until the operations generally used in analytical chemistry admit of greater refinement. Indeed, our analysis would approximate more closely to the truth if we reported the percentage results to one decimal place instead of two. As a matter of fact, two decimals are generally used in technical analyses because we have grown accustomed to the plan, not because it repre-

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[1] A one-gram sample of the clay will contain 0·002 grm. of MgO, which corresponds with 0·0055 grm. of $Mg_2P_2O_7$.

[2] In illustration, see the analyses of tincal by H. Vohl in *Dingler's Journ.*, 201, 165, 1871; and of iron ores by J. C. Welch in *Chem. News*, 52, 32, 1885, to four places (per cent.)! This discussion is resumed later.

[3] H. S. Washington, *Manual of the Chemical Analysis of Rocks*, New York, 24, 1904; M. Dittrich, *Neues Jahrb. Min.*, 2, 69, 1903; W. N. Rae and J. Reilly, *Chem. News*, 114, 187, 200, 1916.

sents the accuracy of the work. The first decimal is supposed to be nearly right; the second is retained in order to keep the first decimal as nearly accurate as possible in calculations made with the analytical data. Under ordinary conditions, therefore, a third decimal is quite out of perspective, while a fourth is an abomination.[1]

Few analytical processes can be depended upon beyond a limit of accuracy represented by 1 in 500; still fewer beyond 1 in 1000. In fact, a method which would enable a real distinction to be drawn between 50·0 and 50·1 per cent. would be considered excellent. As a matter of fact, this degree of accuracy is seldom, if ever, attained in a complex separation. Hence, the statement that 50·13 per cent. of a constituent is present can rarely represent more accurate work than if the result had been simply expressed by the number 50·1 per cent. To quote an illustration by Hinrichs,[2] Berzelius (1826) worked with a balance accurate to 0·01 grm., Ramsay and Aston (1893) worked with a balance accurate to 0·0000001 grm. In seven determinations of the water of crystallisation of borax, Ramsay and Aston found a mean of 0·471677 grm., and Berzelius, 0·4710 grm. per grm. of borax. The individual determinations in the former case varied from 0·471099 to 0·472026. Here then, with a variation in the third decimal, it follows that the fourth and succeeding decimals have no more value than the results determined on the less sensitive balance used by Berzelius.

In some cases, working under special conditions with large amounts of raw materials, it is possible to determine quantitatively certain constituents occurring in amounts below 0·01 per cent. In that case the first significant figure might appear after the second place in the final statement of the results. The determination of these constituents may be useful and important for special purposes, which are not usually industrial.

§ 7. The Weights.

When working to the tenth of a milligram, it is necessary to test an ordinary box of analytical weights in order to find if the weights are consistent among themselves. The errors usually permitted by a standard testing laboratory, before a first-class box of weights can receive its *imprimatur*, are given in the second column of the following table. The third column represents the degree of accuracy of the calibration.

Table I.—Permitted Errors in a Set of Weights.

Weight.	Tolerance.	Values given to	Weight.	Tolerance.	Values given to
200	0·001	0·00001	1 to 2	0·00005	0·000001
100	0·0005	0·00001	0·5	0·00004	0·000001
50	0·0003	0·00001	0·2	0·00003	0·000001
20	0·0001	0·00001	0·05 to 0·01	0·00002	0·000001
5	0·0001	0·00001			

A set of weights which has passed this test will be more accurate than is needed for most analytical work.

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[1] These remarks, of course, have no reference to the analysis of special materials under special conditions where three decimals may be needed to represent the accuracy of the work—for instance, in certain atomic weight determinations; but even here, the value of the result is frequently overrated. See C. Molar, *Rass. Min. Met. Chim.*, 36, 101, 1912.

[2] G. D. Hinrichs, *The Absolute Weights of the Chemical Elements*, St Louis, Mo., 42, 1901

Fairly accurate weights can be purchased for a reasonable sum, and for most gravimetric work the inaccuracies of the better class of weights are negligibly small in comparison with the errors of experiment and the imperfections in the processes of analysis. An analyst, however, will not be satisfied with having his weights *probably* exact enough. He must know that the weights *actually* have the required degree of accuracy. This certainty can only be established by calibrating the weights. The errors introduced by the imperfections of the weights can easily be made less than 0·0001 grm., or 0·01 per cent. The weights should be tested at periodic intervals, say every three or four months. All depends upon the frequency with which the weights are used and who uses them. Faraday[1] has observed: "The balance and weights should be carefully examined at intervals, to ascertain their accuracy, for if they involve unnoticed errors, the experiments made with them may be worse than useless. Some curious conclusions, tending to subvert most important chemical truths, might be quoted as having arisen solely in this way." The weights should be cleaned by wiping them with a camel-hair brush or silk handkerchief. They must not be rubbed.

In special cases, *e.g.* where volumetric apparatus is being calibrated, absolute weights may be required, but for general analytical work absolute weights are not necessary. For instance, suppose that 1 grm. of clay be weighed with a perfect one-gram weight, and exactly 0·1 grm. of silica is obtained. The clay contains 10 per cent. SiO_2. Suppose that the clay be weighed with a one-gram weight which is really 0·9 grm. (called 1 grm.), and that the other weights are consistent. The silica obtained would then weigh 0·09 grm. (called 0·1 grm.). Here, the amount of silica reported in the clay will be the same as before, because $(100 \times 0·09)/0·9 = 10$ per cent. SiO_2. Hence, *if the weights are consistent with one another, their absolute values have no influence on the accuracy of a quantitative analysis.*

Most books on analysis and physics [2] give the *modus operandi* for calibrating a set of weights.

In the course of time the weights gradually decrease in weight, due to "wear and tear." Highly polished weights are less liable to loss by wear than weights with a dull surface.[3] The weights—particularly the smallest—sometimes become heavier. This can usually be traced to the adhesion of dirt to the metal. The following example [4] illustrates the effect of wear on a set of

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[1] M. Faraday, *Chemical Manipulation*, London, 29, 1842.
[2] W. H. Miller, *Phil. Trans.*, 146, 753, 1856; K. L. Bauer, *Zeit. anal. Chem.*, 8, 390, 1869; *Pogg. Ann.*, 137, 103, 1869; R. Bunsen, *Zeit. anal. Chem.*, 6, 1, 1867; T. W. Richards, *Journ. Amer. Chem. Soc.*, 22, 144, 1900; *Zeit. phys. Chem.*, 33, 605, 1900; A. T. Verbeck, *Dingler's Journ.*, 227, 400, 1878; W. Dittmar, *Exercises in Quantitative Analysis*, Glasgow, 1, 1887; W. Ostwald and R. Luther, *Hand- und Hülfsbuch zur Ausführung physiko-chemischer Messungen*, Leipzig, 55, 1902; F. Kohlrausch, *Leitfaden der praktischen Physik*, Leipzig, 50, 1896; W. Crookes, *Phil. Trans.*, 162, 277, 1873; *Chem. News*, 15, 191, 1867; *Select Methods in Chemical Analysis*, London, 687, 1905; H. N. Morse, *Exercises in Quantitative Analysis*, Boston, 26, 1909; P. A. Guye, *Journ. Chim. Phys.*, 14, 25, 1916; N. K. Harvey, *Chem. Eng. Min. Rev.*, 17, 205, 1925; F. C. Eaton, *Journ. Amer. Chem. Soc.*, 54, 3261, 1932; F. H. Hurley, *Ind. Eng. Chem. Anal. Ed.*, 9, 239, 1937. For Benoit's method of calibration, see W. Watson, *A Text-book of Practical Physics*, London, 74, 1906.
[3] The Berichte der Kaiserlichen Normal-Eichungskommission (*Chem. Ztg.*, 10, 1481, 1886) mentions a change, due to internal oxidation within the blowholes of the castings, which was accelerated by the introduction of salt solutions when the weights were gilded. See J. J. Manley (*Phil. Mag.*, (6), 44, 948, 1922) for the protection of brass weights from oxidation.
[4] H. D. Richmond, *Analyst*, 19, 99, 1894; B. Weinstein, *Handbuch der physikalischen Maassbestimmungen*, Berlin, 2, 363, 1888; R. C. Benner, *Mining Sci. Press*, 100, 492, 1911; T. K. Rose, *The Metallurgy of Gold*, London, 460, 1906.

weights which had been in regular use for some years in a laboratory where the need for calibrating the weights was considered superfluous:—

Table II.—Effect of Use on a Set of Weights.

Face value.	Actual value.	Face value.	Actual value.	Face value.	Actual value.
$[10]_a$	Standard	$[1]_b$	0·9989	$[0·1]_b$	0·0982
$[10]_b$	9·9997	$[1]_c$	1·0008	$[0·05]$	0·0485
$[5]$	4·9990	$[0·5]$	0·4982	$[0·02]$	0·0191
$[2]$	1·9991	$[0·2]$	0·1993	$[0·01]_a$	0·0092
$[1]_a$	0·9987	$[0·1]_a$	0·0971	$[0·01]_b$	0·0089

These numbers speak eloquently of the need for checking the weights from time to time. They also show how two analysts might get different results with the same analytical process when possibly one is using faulty weights.[1]

§ 8. The Influence of Inequalities in the Lengths of the Arms of the Balance on the Weighing.

In what precedes, it has been assumed that the two arms of the balance are equal in length. This is not really the case. It is a mechanical impossibility to ensure perfect equality. To find the difference in the lengths of the two arms, add weights of the same nominal value to each pan. The (corrected) weights should be about half the maximum load—say, 50 grms. Bring the balance into equilibrium by means of a rider. Interchange the weights on the pan, and again bring the balance into equilibrium by means of the rider. Call the two weights W and w, and let l and r respectively denote the additional weights required for equilibrium on the left and right sides. Then, on the first weighing, $w + l = W$; and $W = w + r$ on the second weighing. Let L and R respectively denote the lengths of the left and right arms. Then, from the law of levers,

$$L(w + l) = R \cdot W; \text{ and } L \cdot W = R(w + r)$$

Multiply these two expressions together, and reduce by the usual method of approximation for small quantities. We obtain:

$$\frac{R}{L} = 1 + \frac{l - r}{2w}; \text{ and } \frac{L}{R} = 1 - \frac{l - r}{2w} \qquad . \qquad . \qquad . \qquad (1)$$

Suppose that the weighings with corrected weights for an ordinary analytical balance were found to be:

	Left.	Right.

           Left.   Right.

   $[50]$ $[20] + [10]_a + [10]_b + [10] + 0·13$ mgrm.

   $[20] + [10]_a + [10]_b + [10]$ $[50] + 0·19$ mgrm.

Here then $l = -0·13$, and $r = +0·19$ mgrm. Consequently, from the second equation, (1), above,

$$L : R = 1·0000032 : 1$$

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[1] The consistency of the riders can easily be checked from the 0·01-grm. weights, or a standard rider. In the above case the adjustment of the rider has been effected in terms of the given rider. T. K. Rose (*l.c.*) reports that he found some gilded brass riders at the Royal Mint increased in weight from 5·0 to 5·025 mgrms. in six months.

It is then necessary to find the magnitude of the error introduced in a weighing for a known deviation from equality in the lengths of the two arms of the balance. The inequality may be allowed for by multiplying the *apparent weight* by the ratio of the lengths of the two arms, using the ratio $R : L$ or $L : R$ according to the arm with which the weight is connected. This is necessary if the true weight of the object is to be determined.

With the preceding ratio, $L : R = 1·0000032$, a weight w on the left pan will be equivalent to a weight $w \times 1·0000032$ on the right pan. Hence, if a substance on the left pan balances the weight $50 + 0·0001$ grm. on the right pan, the weight of the load is $1·0000032 \times 50·0001 = 50·00026$ grms.—an error of about $0·0005$ per cent. There is therefore no need to apply the correction. Each balance has its own constant $L : R$ for a given load. The numerical value of the ratio varies with different loads.

Most analytical balances do not need an allowance for variations due to inequalities in the lengths of the arms; the lengths are usually made sufficiently exact. When the weights are always placed, say, in the right pan, the correction need not be applied in analytical work, because, although there may be a difference between the apparent and the true weight of the substances which are weighed with the faulty balance, yet this difference is in constant ratio and does not affect the value of the weight ratios. For instance, if R and L respectively denote the lengths of the right and left arms, and the true weights $w_1, w_2, w_3, \ldots$ are represented on the balance by the apparent weights $p_1, p_2, p_3, \ldots$, it follows, from the law of levers, that $w_1 L = p_1 R$; $w_2 L = p_2 R$; $\ldots$ Hence,

$$p_1 = \frac{L}{R} w_1; \quad p_2 = \frac{L}{R} w_2; \quad p_3 = \frac{L}{R} w_3; \; \ldots$$

This means that the value of the ratio of the true weights is the same as the value of the ratio of the apparent weights. That is,

$$w_1 : w_2 : w_3 = \frac{L}{R} w_1 : \frac{L}{R} w_2 : \frac{L}{R} w_3 = p_1 : p_2 : p_3$$

Hence, when two balancing quantities of matter are increased or decreased in the same proportion,[1] they will equally balance one another. Hence, *if the weights be always confined to one pan, the apparent weights will always be increased or decreased in the same ratio, and the results of an analysis will be as accurate on the defective balance as on a balance with arms perfectly equal.* This method of eliminating the error due to the inequality of the arms of the balance presupposes that no weights are placed on the left pan for the purpose of making up a given weight in what may sometimes appear to be the easiest manner, by subtraction.

§ 9. Corrections for the Buoyancy of Air.

It is assumed that, if two things are equal in weight at the same time and place, they contain the same mass or quantity of matter. The weight of a 100-grm. weight is supposed to be 100 times the weight of a 1-grm. weight. This assumption is only true if the two substances have the same volume, or if the comparison be made *in vacuo*. A body weighed in air is buoyed up by a pressure equivalent to the weight of a volume of air which is equal to the volume of the body (Archimedes' principle). Suppose that a 100-grm. platinum weight (sp. gr. 21·5) be balanced against a 100-grm. brass weight (sp. gr. 8·4).

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[1] It is assumed that the same kind of matter is in question, or that the effect of the buoyancy of the air is eliminated. See R. Kempf, *Chem. Ztg.*, 36, 1349, 1912.

It is easy to show that the weight of dry air at, say, 15° C. and 750 mm. displaced by the platinum weight is equal to 0·0056 grm.;[1] while the weight of the air displaced by the 100-grm. brass weight is 0·0143 grm. Hence, if the platinum weight be exactly 100 grm., the brass weight which exactly counterpoises it will not be 100 grm., but $100 + (0·0143 - 0·0056) = 100·0087$ grm. Hence, *the buoyancy of the air produces a sensible effect whenever the volume of the load differs materially from the volume of the weight.*[2]

The arithmetic of the above calculation is summarised in the formula:

$$\text{Corrected weight} = w + wd\left(\frac{1}{s} - \frac{1}{s_1}\right) \qquad . \qquad . \qquad . \qquad (2)$$

where w represents the apparent weight of the object; s, the specific gravity of the object being weighed; s_1, the specific gravity of the weights; and d, the weight of a cubic centimetre of air at the temperature, pressure and humidity prevailing at the time of observation.

EXAMPLE.—A porcelain crucible (sp. gr. 2·3) weighs 7·5392 grms. (w) when the 7-grm. weights are brass ($s_1 = 8·4$) and the 0·5392-grm. weights are platinum ($s_2 = 21·5$). What is the corrected weight of the body when $d = 0·0012$?

With the 7-grm. brass weights,

$$\text{Correction} = 7 \times 0·0012\left(\frac{1}{2·3} - \frac{1}{8·4}\right) = 0·00265 \text{ grm.}$$

and with the 0·5392-grm. platinum weights,

$$\text{Correction} = 0·5392 \times 0·0012\left(\frac{1}{2·3} - \frac{1}{21·5}\right) = 0·00025 \text{ grm.}$$

Consequently, the corrected weight is $7·5392 + 0·00265 + 0·00025 = 7·5421$ grms.

To illustrate the effect of the buoyancy of air on the different precipitates usually weighed in clay analyses, the table opposite may be quoted.

The table shows that when the amount of a precipitate is determined from the difference in the weight of an empty crucible and of the crucible plus residue, and the atmospheric conditions are the same when the two weighings are made, the buoyancy correction is not needed for small precipitates, nor for precipitates with a specific gravity not sensibly different from that of the substance undergoing analysis. In ordinary analytical operations we have to deal with *differences* in weight, not with absolute weights. For instance, an empty platinum dish weighs 63 grms. It is weighed with brass weights (sp. gr. 8·4). A litre of water is evaporated to dryness in the dish and the dish weighed again.

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[1] Thus, the 100-grm. platinum weight has a volume $100 \div 21·5 = 4·65$ c.c. One c.c. of air at 15° C. and 750 mm. weighs 0·0012 grm. Hence, $0·0012 \times 4·65 = 0·0056$ grm. Naturally, all weighings should be reduced to weights *in vacuo*, but the error introduced by taking the apparent weight in air is negligibly small in ordinary analytical work.

[2] The buoyancy correction appears to have been first used by E. Turner about 1830 in determinations of specific gravities and atomic weights (*Phil. Trans.*, **119**, 291, 1829; **123**, 523, 1833). J. J. Berzelius used the correction in some early work, but later regarded the correction as trifling. W. Crookes, *Chem. News*, **15**, 191, 1867; **29**, 29, 1874; C. W. Folkard, *ib.*, **29**, 30, 1874; F. C. Cloud, *ib.*, **35**, 133, 1874; H. R. Proctor, *ib.*, **30**, 255, 1874; *Trans. Newcastle Chem. Soc.*, **2**, 188, 1873; L. L. de Koninck, *Chem. Ztg.*, **18**, 1816, 1894; J. P. Cooke, *Zeit. anal. Chem.*, **23**, 187, 1884; *Chem. News*, **48**, 39, 1883; W. H. Miller, *Phil. Trans.*, **146**, 753, 1856; G. F. Becker, *Liebig's Ann.*, **195**, 222, 1879; J. C. G. de Marignac, *Œuvres Complètes*, Genève, **1**, 44, 1894; *Bibl. Univ.*, **46**, 373, 1843; P. Guye and N. Zachariadès, *Compt. rend.*, **149**, 593, 1122, 1909; A. Scott, *Proc. Chem. Soc.*, **25**, 286, 1909; T. W. Richards and G. P. Baxter, *Journ. Amer. Chem. Soc.*, **32**, 507, 1910; T. Renard and P. A. Guye, *Journ. Chim. Phys.*, **14**, 55, 1916; P. A. Guye, *ib.*, **14**, 83, 1916; W. N. Rae and J. Reilly, *Chem. News*, **114**, 187, 200, 1916. To eliminate the buoyancy correction in weighing bulky glass apparatus use a similar apparatus as a tare—see page 622.

Table III.—Effect of Buoyancy of Air on the Weighings of a Clay Analysis.

Substance weighed.	Specific gravity.	Error per gram of substance weighed.	
		Brass weights.	Platinum weights.
Clay	2·55	0·00033	0·00041
Silica	2·23	0·00039	0·00048
Alumina	3·85	0·00017	0·00028
Ferric oxide . . .	5·12	0·00010	0·00018
Magnesium pyrophosphate .	2·40	0·00036	0·00044
Calcium oxide . .	2·90	0·00027	0·00035
Potassium chloride . .	1·99	0·00046	0·00065
Sodium chloride . .	2·13	0·00042	0·00054
Potassium perchlorate . .	2·52	0·00033	0·00042

The difference in the two weighings represents the solid matter derived from the water.

If there be a considerable difference between the specific gravity of the substance undergoing analysis and that of the ignited precipitate, an allowance must sometimes be made for the different effects of the buoyancy of the air on the different substances. For instance, in determining the amount of sulphur in a sample of pyrites by weighing the precipitated barium sulphate, the error due to the buoyancy of air will be negligibly small. This arises from the fact that the pyrites and the barium sulphate have nearly the same specific gravity and, consequently, nearly the same buoyancy correction. On the contrary, in standardising a solution of silver nitrate by precipitating silver chloride from a given volume of the solution, the buoyancy of air may affect the result by 0·1 per cent.

Effect of Variations of Temperature and Pressure on the Buoyancy of Air.—In the experiment cited above, we assumed that the weight of the empty platinum dish was affected by the air to the same extent before and after the evaporation. It is necessary to examine the validity of this hypothesis. The evaporation takes so long that we cannot reasonably assume that the temperature and barometric pressure have remained constant. Now the weight of a given volume of air depends upon the temperature and pressure. Hence the buoyancy of the air is affected by these two factors.

The brass weights, 63 grms. in the above example, occupy a volume of 7·5 c.c., and the material of the platinum dish occupies a volume of 2·93 c.c. Hence, $7·5 - 2·93 = 4·57$ c.c. more air is buoying up the brass than the platinum weights. The weight of 4·57 c.c. of dry air at 760 mm. and 15° is $4·57 \times 0·001225 = 0·00560$ grm. Consequently, the 63-grm. brass weights really represent 63·00560 grms. Suppose that the barometer falls to 740 mm. and the temperature rises to 25°, the weight of the air will then be $4·57 \times 0·001153 = 0·00527$ grm. Hence, $0·00560 - 0·00527 = 0·00033$ grm. represents the decreased buoyancy of air during the second weighing. Hence, if the dish weighed just 63 grms. on the first weighing, it would weigh 63·00033 grms. on the second weighing.

Assuming the two atmospheric conditions just indicated, and assuming that the observed weights were

Dish plus residue	63·00048 grms.
Empty dish	63·00000 grms.
Residue	0·00048 grm.

2

we might be led to assume that the litre of water contained the equivalent of 0·00048 grm. of solid matter, when in reality it only contained 0·00015 grm. The apparent weight of the dish has increased 0·00033 grm. owing to the decreased buoyancy of the air. If, therefore, we make any pretence to accuracy in the fourth place, we must not only allow for the buoyancy of the air, but we must also allow for the changes in the buoyancy of the air with variations of temperature and pressure.[1] Potash bulbs and calcium chloride tubes, in virtue of their relatively large bulk, might easily lead to errors of 1 per cent., owing to the neglect of the variations in the buoyancy of air under changing atmospheric conditions.

Fresenius, in his classical *Anleitung zur quantitativen chemischen Analyse*, after showing[2] that in analytical work weighings are usually carried to 0·1 mgrm. refers to the correction for the buoyancy of air in these terms: "This defect is so very insignificant, owing to the trifling specific gravity of air in proportion to that of the solid substance, that we generally disregard it altogether in analytical experiments." Fresenius' remark is also true of analytical practice at the present day, but it is equally true that weighings below 0·0005 grm. are then of no particular value, and this altogether apart from the inaccuracies mentioned on page 11 arising from the particular character of the analytical process.

Effect of Variations of Humidity on the Buoyancy of the Air.—The humidity of the air is also constantly changing. We must therefore inquire what effect this has on the buoyancy of the air.[3] The preceding calculations were referred to *dry* air at the temperatures and pressures indicated. As a matter of fact, the buoyancy of moist air is less than that of dry air; hence, the correction for moist air will be less than for dry air. In illustration,[4] a crucible kept in the balance case during the summer months—July and August—showed the following variations in weight:—

Table IV.—Effect of Humidity of Air on Weighings.

	Weight in air.	Weight corrected for buoyancy of moist air.	Weight corrected for buoyancy of dry air.
	grms.	grms.	grms.
Maximum	39·35659	39·37046	39·37061
Minimum	39·35601	39·37040	39·37052
Mean	39·356362	39·370437	39·370562
Deviations from mean . . {	+ 0·000228 − 0·000352	+ 0·000023 − 0·000037	+ 0·000048 − 0·000042

[1] THE EFFECT OF GRAVITATION ON THE BUOYANCY OF AIR.—Strictly speaking, the weight of a litre of dry air at 760 mm. differs in different localities. This is not merely because the action of gravity on a litre of air is different in different places, but because a pressure of 760 mm. of mercury varies with the intensity of gravitation. Thus, the intensity of gravity at Greenwich is to that at Paris as 3457 : 3456. Hence, if a litre of dry air at Paris weighs 1·2932 grms., a litre of air at Greenwich will weigh 1·2936 grms. under the same conditions of pressure and temperature. Hence, the effect of gravitation on the buoyancy correction is negligible. The small difference in the buoyancy of air in the two places has no appreciable effect when applied to particular cases.

[2] R. Fresenius, *Quantitative Chemical Analysis*, London, 1, 18, 19, 1876.

[3] The fallacy of assuming that the air inside a balance case is dry simply because a couple of jars of calcium chloride or of sulphuric acid are in the case will appear from page 7.

[4] O. Kuhn, *Chem. Ztg.*, 34, 1097, 1108, 1910; R. Kempf, *ib.*, 36, 1349, 1912.

Hence, the average effect of variations in moisture is somewhere near 0·00013 grm. In one of the experiments, a variation of 10 per cent. in the humidity of the air only altered the corrected weight 0·00003 grm. That is outside the range of weighings conducted to 0·1 milligram. Applying our test—the errors in weighing should fall within the limits of experimental error due to the analytical process—it follows that it is necessary to allow for variations in the buoyancy of air due to variations of temperature and pressure when the weighings are conducted to the tenth of a milligram, but further variations due to humidity can be neglected under these conditions.

It is generally convenient to assume that the average weight of a cubic centimetre of moist air is 0·0012 grm.[1] Remembering that for general purposes the weights are calibrated in air, and that we assume the buoyancy is a constant corresponding with the weight 0·0012 grm. per c.c., we are only concerned with variations in the buoyancy of the object being weighed.[2] In that case, we use, in place of formula (2) on page 16.

$$\text{Corrected weight} = w + 0·0012w/s \qquad . \qquad . \qquad (3)$$

By making $w = 1$ grm. and plotting the corrected weight for different values of s (specific gravity), we get the curve shown in fig. 6. This enables the correction for a given weight of substance to be seen at a glance.
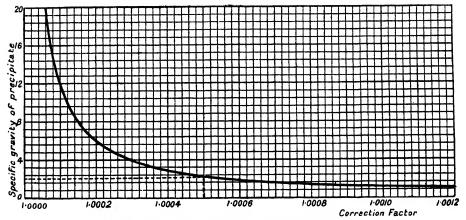
FIG. 6.—Buoyancy Correction for Substances of Different Specific Gravity.

EXAMPLE.—A silica "precipitate" weighs 0·6021 grm. What is the corrected weight if the specific gravity of calcined silica is 2·25? From the diagram (dotted lines), we see that the correction factor is 1·0005 per grm. Hence, 1·0005 × 0·6021 = 0·6024 grm. is the corrected weight.

§ 10. Summary.

The important lesson we learn from this chapter is that in analytical chemistry, as well as in other work involving delicate measurements, it is always advisable to make at least a rough estimate of the influence of the various

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[1] The density of moist air can be calculated from the expression $d = d_0(P - 0·378p)/P$, where d is the density of the moist air, d_0 that of dry air at a barometric pressure of P mm., and p is the pressure of water vapour in the air. The value of p is determined from tables giving the maximum pressure of water vapour corresponding with the dew point of the air.
[2] W. Dittmar, *Exercises in Quantitative Chemical Analysis*, Glasgow, 8, 1887; P. Schott-länder, *Zeit. phys. Chem.*, 16, 458, 1895.

sources of error on the final result.   These errors can only be neglected when their effect is small in comparison with the error derived from other sources. The chief sources of error commonly introduced in the balance room are those arising from: (1) Variations in the zero point of the balance; (2) Inconsistent weights; (3) Inequalities in the lengths of the arms of the balance; and (4) The buoyancy of the air.   We have seen that in results making any pretence to accuracy to the "second decimal" or to the " $\frac{1}{10}$th milligram"—

(1) The zero point of the unloaded balance should be determined and the weighing made by one of the methods given on pages 7 to 9.

(2) The weights should be calibrated and periodically checked (pages 12 to 14) for consistency among themselves.

(3) The error due to the inequality in the arms of the balance can be neglected in ordinary analytical work (page 14).

(4) The correction of the weighings for the buoyancy of air is necessary when the determination involves the weighing of substances with appreciably different specific gravities (page 17).   In general analytical work this correction can be neglected, since the resulting error is overshadowed by the errors associated with the preparation of the precipitates for the balance.

CHAPTER II.

THE MEASUREMENT OF VOLUMES.

§ 11. Volumetric and Gravimetric Processes of Analysis.

MEASUREMENTS with a good balance and weights can readily be conducted with a precision far greater than is needed for general analytical work. It has been pointed out that the errors involved in the preparation of a troublesome precipitate for weighing will impair the value of an exact weighing. The measurement of volume, in volumetric analysis, may not be so precise and reliable as the measurement of weight, yet the results of volumetric processes, based on suitable reactions, are frequently more trustworthy than gravimetric processes, because the method of preparing the substance for the measurement by volumetric processes is less liable to error.

There is a prejudice in some minds against volumetric processes. It is claimed that in general "there is a lack of precision in volumetric analysis." In many cases the prejudice arises from the fact that some essential precautions have been neglected; in other cases there may be an intrinsic weakness in the method itself. There is also some confusion possible in the different systems of measurement. With proper precautions many volumetric processes are excellent, and, for technical analyses, invaluable. Indeed, in technical work, where time is an essential factor, volumetric processes are used in preference to gravimetric wherever expedient.[1] It is important to have a clear idea of the precautions necessary for a high degree of accuracy, in order that errors of vital importance may be eliminated. The need for the "analytical perspective," mentioned on page 11, is here of great moment.

§ 12. The Influence of Variations of Temperature.

The volume of a solution depends on the temperature. The higher the temperature, the greater the volume of a given weight of a solution. A glass measuring vessel also has a greater capacity the higher the temperature. Although the level of a solution in, say, a litre flask may rise above the litre mark as the temeprature rises, this naturally occurs because the expansion of the water more than counterbalances the increased capacity of the flask. If the expansion of the glass were greater than the expansion of the solution, with rise of temperature the level of the liquid in a standard flask would sink below the mark on the neck of the flask. The liquid would appear to contract. The volume measured at any temperature, different from the standard temperature, is the joint effect of the changed capacity of the flask and the changed volume of the liquid.

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[1] R. Hasenclever, *Ber.*, 33, 3827, 1900.

Let us take the coefficient of cubical expansion of glass [1] to be 0·000025; and Thiesen, Scheel and Disselhorst's [2] values for the volume of water at different temperatures indicated in the subjoined table (Table V.). The

Table V.—Volume and Density of Water at Different Temperatures.

Temp.	Volume.	Density.	Temp.	Volume.	Density.
0	1·0001324	0·9998676	20	1·0017728	0·9982303
1	1·0000734	0·9999266	21	1·0019853	0·9980186
2	1·0000320	0·9999680	22	1·0022083	0·9977966
3	1·0000078	0·9999922	23	1·0024414	0·9975645
4	1·0000000	1·0000000	24	1·0026847	0·9973225
5	1·0000082	0·9999918	25	1·0029378	0·9970708
6	1·0000320	0·9999680	26	1·0032006	0·9968097
7	1·0000707	0·9999293	27	1·0034729	0·9965391
8	1·0001241	0·9998759	28	1·0037546	0·9962594
9	1·0001917	0·9998084	29	1·0040455	0·9959708
10	1·0002730	0·9997271	30	1·0043456	0·9956732
11	1·0003678	0·9996324	31	1·0046546	0·9953670
12	1·0004756	0·9995246	32	1·0049724	0·9950522
13	1·0005962	0·9994041	33	1·0052989	0·9947290
14	1·0007292	0·9992713	34	1·0056341	0·9943975
15	1·0008744	0·9991264	35	1·0059777	0·9940578
16	1·0010314	0·9989697	36	1·0063297	0·9937101
17	1·0012000	0·9988014	37	1·0066899	0·9933545
18	1·0013799	0·9986220	38	1·0070584	0·9929911
19	1·0015709	0·9984315	39	1·0074349	0·9926200

number of cubic centimetres of water which must be subtracted from or added to 1000 c.c. of water to give the volume of distilled water at $t°$, in order to fill a litre flask calibrated at 15°, is indicated in the following table [3] (Table VI.). The data have been calculated from the preceding Table V. [4]

Table VI.—Reduction for the Change of the Apparent Volume of a Litre of Water with Temperature. (Standard temperature = 15°.)

Temp.	0	1	2	3	4	5	6	7	8	9
0	..	..	..	..	..	+ 0·63	+ 0·62	+ 0·60	+ 0·57	+ 0·53
10	+ 0·48	+ 0·41	+ 0·32	+ 0·22	+ 0·12	Zero.	− 0·13	− 0·28	− 0·43	− 0·60
20	− 0·77	− 0·96	− 1·16	− 1·37	− 1·58	− 1·81	− 2·05	− 2·30	− 2·57	− 2·82
30	− 3·10	− 3·38	− 3·67	− 3·97	− 4·28	− 4·60	− 4·93	− 5·27	− 5·61	− 5·96

[1] The value for glass used in volumetric work ranges from 0·000023 to 0·000028, according to the nature of the glass. The figure 0·000026 is often used as the average value, but the error introduced by these variations is negligibly small.

[2] M. Thiesen, K. Scheel, H. Disselhorst, *Wiss. Abh. phys. tech. Reich.*, **3**, 1, 1901.

[3] For a table based upon some older data, see P. Casamajor, *Journ. Amer. Chem. Soc.*, **1**, 188, 1876; **2**, 19, 1877; *Chem. News*, **35**, 160, 170, 1877; **38**, 137, 1879. See also W. Schlösser, *Zeit. angew. Chem.*, **17**, 953, 977, 1004, 1904; **21**, 2161, 1908; *Chem. Ztg.*, **29**, 509, 1904; *Zeit. anal. Chem.*, **46**, 392, 1907; H. L. Payne, *Journ. Anal. App. Chem.*, **6**, 326, 1892.

[4] The standard temperature for British volumetric glassware was fixed in 1934 at 20° C. (international temperature scale); see *British Standards Institution, Report* No. 554, 1934. With this new temperature of reference, another table can readily be compiled from the above. For instance 15° becomes + 0·77 and 25° − 1·04.

The use of Table VI. may be illustrated by the following examples:

EXAMPLES.—(1) 25 c.c. of water are measured in a burette at 28°: what is this volume at the standard temperature, 15°? From Table VI. it follows that since 1000 c.c. require a correction of -2.57 at 28°, 25 c.c. will require a correction of -0.06. Hence, $25 - 0.06 = 24.94$ c.c. is the required volume.

(2) What is the volume at 15° of a litre of water measured in a flask at 10°, and also at 18°? From the table, the correction for 1000 c.c. at 10° is $+0.48$, and at 18°, -0.43. Hence the required volumes are $1000 + 0.48 = 1000.48$ c.c. at 15°, and $1000 - 0.43 = 999.57$ c.c. at 18°.

Table VI. thus represents the volume which a litre of water alters in a glass vessel when its temperature changes from 15°. If the prevailing temperature does not differ by more than, say, 3° from the standard temperature, the changes may be ignored. The corresponding corrections for 0·1N and 0·2N solutions differ so little from the values for pure water that Table VI. can still be used for such solutions.[1] Normal and still more concentrated solutions require special tables, since the deviations are then greater—see, for example, Tables XI. and XXXI.

In weighing a litre of water in a glass vessel, the most important source of error arises from the variation of temperature. A difference of 1° will give a difference of 0·18 c.c., corresponding with 0·018 per cent. A variation of the barometer of 15 mm. of mercury will affect the measurement by 0·001 c.c. Hence, barometer variations can generally be neglected.

§ 13. The Litre and its Subdivisions.

Owing to the great difficulty in measuring directly the relation between cubic capacity and the unit of length, the International Committee of Weights and Measures,[2] in 1880, recommended that the word "litre" be used to represent "the volume of a kilogram of pure water at its maximum density"; and in 1901 this definition was amplified to read: "The litre is the volume occupied by the mass of one kilogram of pure water at its maximum density and under normal atmospheric pressure."[3] The litre so defined is a little larger—about 0·027 c.c.—than a cubic decimetre. Evidently, then, the cubic centimetre is not really the thousandth part of a litre, but a little smaller than the thousandth part.

In view of this discrepancy, the Joint Committee for the Standardisation of Scientific Glassware unanimously recommended[4] that "the recognised international metric units—the 'litre' (l.) and 'millilitre' or thousandth part of the litre (ml.)—shall be used as the standard units of volume, and that standard volumetric glassware shall be graduated in terms of these units and marked 'ml.' instead of 'c.c.'"

Since, as stated above, 1 litre $= 1000 \cdot 027$ c.c., "the difference between the cubic centimetre and the millilitre is so small as to be negligible for ordinary volumetric glassware; the difference in capacity between a 1000 c.c. flask

[1] H. Pellet, *Ann. Chim. anal.*, 20, 97, 1915.

[2] *Procès-Verbaux Comité Internat. Poids et Mesures*, 30, 1880; 175, 1901; P. Chappius, *ib.*, (2), 2, 72, 1903; J. M. de Lepinay, *Journ. Phys.*, (3), 5, 477, 1897; D. Mendeléeff, *Proc. Roy. Soc.*, 59, 143, 1895; W. Schlösser, *Zeit. angew. Chem.*, 16, 960, 1903; *Report Internat. Cong. Applied Chem.*, 6, 1, 1906.

[3] The temperature of maximum density is not defined—it appears to be a shade under 4° C.—nor does the definition make any reference to weighing *in vacuo*. In the calculations it is assumed the weighings are *in vacuo*.

[4] *Report* No. 1, 1, 1924. See also *Brit. Standards Inst. Report* No. 501, 1933.

and a litre flask, for example, is less than the observational errors liable to arise in the ordinary use of either flask." [1] Consequently, the change-over from cubic centimetre to millilitre has not been made in the revision of this work, particularly as a consistent nomenclature has been used throughout.

Unfortunately, there are a number of different litres used in laboratories. The more important are the following:—

(1) *Normal litre.*—The volume of 1000 grms. of air-free water (weighed *in vacuo*) at +4°. If, therefore, the litre flask is marked correctly at +15°, this means that at a temperature of 15° the capacity of the flask is the same as the volume of a kilogram of water at +4°. This is the normal, true or international litre used in this work.[2]

(2) *Mohr's litre.*—The flask contains the same number of grams of water (free from air) at the specified temperature as the number of cubic centimetres or grams stated on the flask. For instance, the Mohr's litre is "the volume occupied by a kilogram of water, at 17·5°, when weighed in air with brass weights." [3]

The Joint Committee also suggested [4] that in future the unit of volume on Mohr's system shall be designated by the letters "G.W.A.," this being an abbreviation for "grammes of water in air." The Committee defines the G.W.A. unit as follows:— "A quantity of water which weighs 1000 grammes in air of density 0·0012 grm./ml. when weighed against brass weights of density 8·4 grm./ml. occupies a volume of 1002·021 ml. at 60° F." This volume differs from 1002 ml. only by two parts in a hundred thousand, which is negligibly small in comparison with the tolerances allowed on volumetric glassware and the accuracy attainable in the ordinary use of such glassware. Hence the Committee on grounds both of convenience and precision have adopted the definition . . . "1000 G.W.A. = 1002 ml."

It matters very little, in analytical work, which litre be adopted, but it is necessary to keep rigorously consistent to the one system in all volumetric apparatus such as burettes and pipettes. This matter is serious enough to require emphasis, since apparatus, if not specifically ordered, may be supplied by the dealers, at different times, graduated according to different systems, and mixed graduations may thus be introduced on one bench. The figures quoted above show the magnitude of the error which would be introduced in confusing the different systems.

Standard Temperature.—It would be exceedingly inconvenient, if not impossible, to weigh exactly a kilogram of water at +4° *in vacuo*; nor is it practicable to work at +4°. Some other more convenient temperature must be selected, and the necessary corrections made. In this work, 15° is supposed to be the standard temperature.[5] This temperature is recommended by the Kaiserliche Normal-Echungskommission (K.N.E.K.),[6] Berlin; 17·5° was

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[1] *Report* No. 1, 4, 1924.

[2] At 15°, therefore, this litre does not represent 1000 grms. of water, but rather 999·1264 grms.

[3] F. Mohr, *Zeit. anal. Chem.*, 7, 285, 1868; H. Beckurts, *Die Methoden der Massanalyse*, Braunschweig, 42, 1910. Mohr made no allowance for variations in the atmospheric conditions.

[4] *Report* No. 1, 6, 1924.

[5] The tables can, of course, be modified for other appreciably different climates. If the flasks, etc., were cooled for weighing, there would be a danger of the deposition of moisture on their surface.

[6] *Zeit. angew. Chem.*, 6, 557, 1893; L. A. Fischer, *Journ. Amer. Chem. Soc.*, 20, 912, 1898; C. Laurent, *Bull. Soc. Chim. Nord France*, 1, 20, 1891; H. Ost, *Chem. Ztg.*, 14, 1747, 1899; W. Fresenius, *Zeit. anal. Chem.*, 30, 461, 1891; A. Classen, *Theorie und Praxis der Massanalyse*, Leipzig, 64, 1912.

recommended by Mohr,[1] and by Treadwell; 18°, by Lundén;[2] and 20° is recommended by Wagner,[3] and the U.S. Testing Laboratory.[4] The Chemical Divisional Council of the British Standards Institution has recently decided to adopt 20° (international temperature scale) as the standard temperature for British standard volumetric glassware.[5] The right choice should be determined by the prevailing temperature of the laboratory. Apparatus intended for working in warm climates may be graduated for 20°, 22°, or 25°; and 15° or 17·5° for cooler climes.

From the discussion on page 24 it is easy to find what amount of water must be weighed at any given temperature to have a volume equal to the volume of a kilogram of water at $+4°$, given the specific gravity of air, say, 0·0012 kilogram per litre; the specific gravity of the brass weights, 8·4; the coefficient of cubical expansion of glass, 0·000025. Let S denote the specific gravity of water at $t°$—Table V. *To find what amount of water at any specified temperature must be weighed in air with brass weights to give a normal litre.* Since a kilogram of water at $+4°$ weighed *in vacuo* occupies 1 litre, it follows from the discussion on page 15 that a litre of water will weigh

$$w = S - 0·0012\left(1 - \frac{S}{8·4}\right) \text{ kilogram} \qquad . \qquad . \qquad . \qquad (1)$$

when weighed in air with brass weights. But a flask exactly 1 litre at 15° has a capacity of $1 + 0·000025(t - 15)$ litres at $t°$. Hence, it is necessary to weigh

$$W = [1 + 0·000025(t - 15)]\left[S - 0·0012\left(1 - \frac{S}{8·4}\right)\right] \text{kilogram} \qquad . \qquad (2)$$

at $t°$ in order to find what the capacity of the flask would be if the water had been weighed *in vacuo* at 4° with brass weights.

EXAMPLE.—What amount of water must be weighed in a flask at 15° in order that a mark can be made on the neck of the flask to represent the volume of a kilogram of water weighed at 4° *in vacuo*? From Table V., page 22, $S = 0·9991264$, and $t = 15$. Substitute these numbers in the preceding formula (2). We get a weight 0·998069 kilogram. In practice, therefore, the flask is counterpoised on the balance, a kilogram weight is placed on the right pan, and $1000 - 998·069 = 1·931$ grms. on the left pan. When the flask (on left pan) has sufficient water to restore equilibrium, the volume of the water in the flask represents the volume of a kilogram of water at 4° when weighed *in vacuo*.

In order to avoid the labour of calculation, Schlösser[6] has computed a table of values ranging from 5° to 30·9°, referred to air and water at 15°, and the barometer at 760 mm.

§ 14. Meniscus, Parallax Errors and Burette Floats.

Parallax Errors.—In reading the level of liquids in burettes and pipettes, the lower boundary of the dark meniscus is taken as the normal reading. Parallax errors must be carefully watched. If the eye be not in the same

[1] F. Mohr, *Lehrbuch der chemisch-analytischen Titriermethoden*, Braunschweig (H. Beckurts' edition), 42, 1910; F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, **2**, 432, 1911.

[2] H. Lundén, *Svensk Kem. Tids.*, **24**, 96, 1912.

[3] J. Wagner, *Zeit. phys. Chem.*, **28**, 193, 1899.

[4] *Circular, Bureau of Standards*, **9**, 2, 1904; N. S. Osborne and B. H. Veazey, *Bull. Bur. Standards*, **4**, 553, 1908.

[5] *Report* No. 554, 1934.

[6] W. Schlösser, *Zeit. angew. Chem.*, **16**, 960, 1903; *Chem. Ztg.*, **27**, 4, 1904.

horizontal plane as the meniscus, *BB'* (fig. 7), the reading may be either too high or too low. For instance, if the eye be looking in the direction *AA'* the reading will be too high; and if in the direction *CC'*, the reading will be too low. The direction *BB'* gives a correct reading free from parallax. In the diagram, the correct reading is 30·0 c.c.; the two readings affected by parallax errors are *AA'*, 30·3 c.c., and *CC'*, 29·85 c.c. If the mark to be read encircled the burette, the eye would see only one horizontal line when at the proper
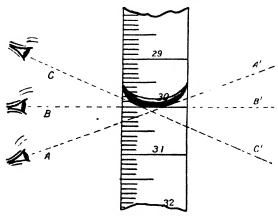
Fig. 7.—Meniscus Errors.

level for reading. The marks rarely encircle the burette and some auxiliary is therefore needed.[1]

Meniscus Screens.—The level of the meniscus is made more distinct by placing the burette so that it has a white wall as background and shading the light from below by holding two fingers behind the burette just below the meniscus,[2] or Mohr's simple and effective plan of holding a piece of paper, partly blackened, with the blackened portion just below the meniscus, as illustrated in fig. 8.[3]

Burettes made to Accentuate the Meniscus.—Rohrbeck's burettes (fig. 9), made with a flat instead of a circular tube, make errors due to parallax less likely. The meniscus with these burettes comes out very clearly. Schellbach[4] recommends the use of burettes with two narrow white enamel longitudinal strips separated by a dark-coloured (blue) strip down the back of the burette. A fine point appears symmetrically placed between the strips at the boundary of the meniscus (fig. 10)[5] when the eye is in the right position for

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[1] A reading lens is often a great help in exact work.

[2] B. Reinitzer, *Zeit. angew. Chem.*, 7, 547, 573, 643, 1894.

[3] J. H. M'Mahon (*Chem. News*, 45, 109, 1882; F. A. Gooch, *Amer. J. Science*, (3), 44, 239, 1892; P. Kusnetzoff, *Zeit. anal. Chem.*, 46, 515, 1907; A. Prinzl, *Deut. Amer. apoth. Ztg.*, 4, 637, 1885; F. Köhler, *Brit. Pat.*, No. 10936, 1903) recommends a small mirror on the surface of which are pasted two parallel strips of black paper each, say, 2 in. long and ¼ in. wide, with a space about ¼ in. wide between them. When reading, place the mirror behind and in contact with the burette, in such a position that the reflection of the eye can be seen in the space between the strips of paper. This ensures the eye being at right angles to the burette; J. F. Sacher, *Chem. Ztg.*, 35, 622, 1911.

[4] P. Schellbach, *Chem. Ztg.*, 8, 1515, 1885; J. Milbauer, *ib.*, 35, 419, 1911; J. F. Sacher, *ib.*, 35, 622, 1911; G. Goetze, *Zeit. anal. Chem.*, 50, 373, 1911. It will be noticed that Schellbach's burette does not read the lowest level of the meniscus.

[5] Vernier burettes—C. Meinecke, *Chem. Ztg.*, 16, 792, 1892; A. F. Reid, *Chem. News*, 65, 125, 1892.

a reading.   If the eye be too high or too low, the point does not appear sharp, but is more or less ill-defined and blunted.   A few minutes' trial will soon show that there is a fairly wide range of height and depth within which the point
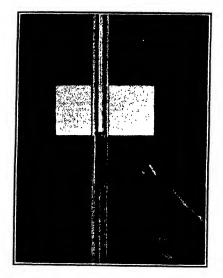
FIG. 8.—Mohr's Shaded Screen.   FIG. 9.—Rohrbeck's Burette.

Eye too low.   Eye correct.   Eye too high.

FIG. 10.—Meniscus Errors.

would be adjudged correct for a reading.   In spite of this, these burettes are much used.[1]

Göckel's screens [2] (fig. 11) are quite satisfactory for reading the level of opaque liquids, and for avoiding the parallax errors in other solutions.   The Göckel screen is a blackened clamp which grips the burette two or three milli-metres below the level of the meniscus.   The blackened part cuts off extraneous light from below, and leaves a sharp boundary-line at the meniscus.   A sheet of white paper held behind the burette or fixed to the Göckel's screen, as shown in the diagram, still further emphasises the meniscus.   A reading is made with the eye placed so that the front and back edges of the screen coincide.

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[1] Some testing stations refuse their *imprimatur* on these burettes.
[2] H. Göckel, *Chem. Ztg.*, **27**, 1036, 1903; J. Bergmann, *ib.*, **11**, 853, 1898; G. Lunge, *Zeit. angew. Chem.*, **17**, 198, 1904; G. Kottmayer, *Zeit. anal. Chem.*, **30**, 327, 1891; L. S. Pratt, *Journ. Amer. Chem. Soc.*, **37**, 1730, 1915; W. P. White, *ib.*, **57**, 332, 1935.

Burette Floats.—Cylindrical floats arranged to swim on the surface of the liquid in the burette are marked so that the juxtaposition of the mark on the float with the graduations of the burette gives the required reading. The floats are supposed to eliminate dangers from parallax errors and troubles with the meniscus. The ordinary Erdmann's float [1] is a plain cylinder. It has a tendency to stick to the inner walls of the burette and is also inclined to assume an oblique position in the burette if it is not perfectly weighted. The simple float has therefore been condemned. Volhard placed a number of glass spines over the outer wall of Erdmann's float with the idea of preventing the
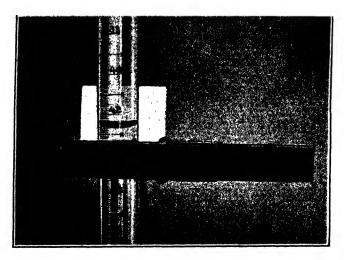
Fig. 11.—Göckel's Burette Screen.

float sticking to the inner walls of the burette. Beutell's floats [2] give good results provided that they are so weighted as to swim vertically in the liquid. It is possible to read to 0·01 c.c. in a good burette with a good Beutell's float—provided the bore of the tube is not too wide and the burette is suitably graduated. This float sticks to the side of the burette when the burette is emptied and therefore, when the burette is to be refilled, the float must be taken out, carefully cleaned, and returned to the liquid. Diethelm [3] added an extra bulb to Beutell's float to make the removal of the float unnecessary every time the burette is refilled. In Rey's float, a small second bulb projects above the surface of the liquid and carries a mark. Hence, this float can be used for opaque liquids and dark-coloured solutions. [4] The mark on the bulb above

[1] O. L. Erdmann, *Journ. prakt. Chem.*, (1), **71**, 193, 1857; J. Volhard, *Leibig's Ann.*, **176**, 240, 1875; A. Schulze, *Zeit. anal. Chem.*, **21**, 167, 1882; **26**, 626, 1887; A. Gawalovski, *ib.*, **38**, 237, 1899; **22**, 240, 1883; R. Benedikt, *Chem. Ztg.*, **16**, 217, 1892; N. Wolff, *ib.*, **13**, 389, 1889; F. Musset, *Pharm. Centr.*, (3), **16**, 459, 1885. C. Meissner (*Chem. Centr.*, (3), **18**, 135, 1887) has a float fitted with a thermometer.

[2] A. Beutell, *Zeit. angew. Chem.*, **2**, 8, 1889.

[3] B. Diethelm, *Chem. Ztg.*, **26**, 607, 1902; H. Rey, *Ber.*, **24**, 2098, 1891; L. W. Andrews, *Zeit. anorg. Chem.*, **26**, 179, 1901; J. Wagner, *Zeit. phys. Chem.*, **28**, 193, 1899; P. Kreitling, *Zeit. angew. Chem.*, **13**, 829, 990, 1900; **15**, 4, 1902; W. Schlösser, *ib.*, **16**, 953, 962, 977, 1004, 1903; G. Lunge, *ib.*, **13**, 936, 1900; H. Thiele, *Zeit. öffent. Chem.*, **6**, 172, 1902.

[4] With highly coloured solutions, such as permanganate, a simple and effective plan is to hold a few inches of lighted taper behind the meniscus. By adjusting the position of the flame the lower edge of the meniscus can clearly be seen.

the surface of the liquid is used for reading the differences of level of the liquid in the burette. The principal objection to floats is the difficulty in getting them properly weighted. A float which works satisfactorily with one liquid may be quite unsuited for another. There is an element of chance in purchasing a good float.[1]

§ 15. The Calibration of Standard Flasks.

Just as in gravimetric work the accuracy of the weights is not to be taken on trust, so must exactness of the measuring apparatus in volumetric analysis be established by trial. It is not at all uncommon to find that the weights in a laboratory have been the subject of wise scepticism, while the volumetric instruments have been accepted with blind faith, and conversely. It matters little what litre be adopted as a standard, but *it is of the greatest importance to have the pipettes, burettes and measuring flasks rigorously consistent with one another*. The litre flask, for example, must hold 10 times as much as the 100 c.c. flask; 20 times as much as the 50 c.c. pipette; 200 times as much as the 5 c.c. pipette; etc.

The National Physical Laboratory calibrates all types of volumetric glassware, although some chemists prefer to test or calibrate their own apparatus. True, this may not be done with the precision exercised by officials accustomed to the work with every facility close at hand; but pipettes and burettes may be quite satisfactorily calibrated with the regular laboratory outfit.[2] The calibration of litre flasks needs a balance large enough to weigh a kilogram of water, and sensitive enough to indicate 0·02 grm. An ordinary analytical balance will suffice for small flasks.[3]

A litre flask with a long cylindrical neck, between 14 and 20 mm. in diameter, is thoroughly cleaned [4] and dried. The empty dry flask is balanced by a suitable tare. Fill the flask with distilled water until the lowest point of the meniscus is in the same horizontal plane as the mark on the neck. Let the flask stand in the balance case until the temperatures of the air and water are within 1°. Adjust the level of the water in the flask. Remove any excess of

[1] For the use of the nonius or vernier with burettes, see F. Friedrichs, *Zeit. angew. Chem.*, 29, 343, 1916.

[2] As a rule, the analytical chemist cannot spare much time for calibrating his apparatus, and the cost in time will be greater than the charge made by the National Physical Laboratory, which has every facility for doing the work quickly.

[3] H. N. Morse and T. L. Blalock, *Amer. Chem. Journ.*, 16, 479, 1894; A. Gawalovski, *Chem. Centr.*, (3), 10, 236, 1879; A. Démichel, *Rev. Anal. Chim.*, 5, 1897; A. Mulder, *Chem. Weekblad*, 5, 830, 1908.

[4] CLEANING VOLUMETRIC APPARATUS.—Grease is the great foe of accuracy in volumetric work. Thorough freedom from grease is very important. The smallest trace of grease may distort the meniscus and alter the amount of water retained as a film on the glass. The error so introduced may amount to 0·01 to 0·04 per cent., according to the method used in cleaning the vessel. To clean flasks, pipettes or burettes, wash the vessel thoroughly with a concentrated aqueous solution of caustic soda; rinse with water; wash with a solution of chromic acid or potassium dichromate in sulphuric acid; and thoroughly rinse with distilled water. Flasks, etc., seem gradually to acquire a greasy film on their inner surface while in use. In some cases, the grease can be traced to the contamination of the distilled water by the oily packing between the "worm" and "still-head" of the still. If grease be absent, the surface of the glass will remain covered with a continuous film of water until all is removed by evaporation. If the water collects in drops instead of adhering as a continuous film, the vessels are greasy and want cleaning. A rapid method for removing grease is to wash thoroughly with *pure* acetone, allow to drain, and then wash with distilled water. W. O. Atwater and C. D. Woods, *Journ. Anal. App. Chem.*, 1, 373, 1887; C. Mohr, *Chem. Ztg.*, 11, 561, 1887; W. Glenn, *Journ. Amer. Chem. Soc.*, 22, 302, 1900; J. Walz, *Dingler's Journ.*, 207, 427, 1873. M. Vandevyver (*Rev. Anal. Chim.*, 5, 1897) shows that the errors due to variations in surface tension are reduced to a minimum if perfectly clean vessels are used.

water by a piece of capillary tube. Do not allow drops of water to adhere to the interior of the neck of the flask; if any should be present, they may be removed by means of a piece of filter paper tied round the end of a glass rod.   Weigh the flask and contents. Take the temperature of the water with a thermometer reading to 0·1°. The mean of three weighings may be taken as the correct value.

Suppose the mean of three weighings to be 998·95 grms. (brass weights in air); temperature of the water 15°; barometer, 750 mm. Since the average weight of a litre of moist air at 15° and 750 mm. is 1·20 grms., the water in the flask—by formula (3), page 19—will weigh $998 \cdot 95 + 1 \cdot 20 = 1000 \cdot 15$ grms. The brass weights have probably been adjusted for weighing in air. In that case, we neglect the air displaced by the weights. If the weights have been reduced to weight *in vacuo*, we must make an allowance as indicated on page 16.[1] It is not necessary to have the temperature of the water just 15°. When we know the weight of a given volume of water under any conditions of temperature, it is easy to calculate the corresponding amount of water for any standard temperature from Table V., page 22.

The "error" allowed by most of the testing stations for measuring flasks is as follows:—

Capacity	50	100–250	300–500	500–1000	2000 c.c.
Permitted error (Contain) .	0·05	0·1	0·15	0·3	0·5 c.c.
Permitted error (Deliver) .	0·1	0·2	0·3	0·6	1·0 c.c.

§ 16. The Drainage or Afterflow from Measuring Vessels.

The drainage of measuring apparatus is of great importance. Schlösser [2] has established a relation between the time the discharge is stopped and the amount—afterflow—subsequently drained from the sides. The drainage is greater the more rapid the discharge of the liquid. When the discharge from a burette was 0·7 c.c. per second, the afterflow during the first two minutes after stopping the outflow was found to be about 0·05 c.c. When the time of the discharge from the burette was changed from 65 to 125 seconds, a decrease of 0·05 c.c. in the volume of the afterflow was obtained. Hence, if 0·05 c.c. of the standard solution will appreciably affect the result, it is necessary to work under standard conditions, and pay attention to the time of outflow of all apparatus marked "Deliver" ("Ausguss")—burettes, pipettes, flasks, etc.

The rate of outflow for burettes and measuring pipettes is limited by the size of the tip, and it is usual to make the tip so that the time of outflow is not greater than three minutes, nor less than the numbers indicated in the following table:—

Length graduated	65	60	55	50	45	40	35	30	25	20	15 c.c.
Time of outflow .	140	120	105	90	80	70	60	50	40	35	30 secs.

When titrating and standardising burettes, it is well to wait a couple of minutes [3] before every reading in order to give the sides time to drain.

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[1] An error of 0·1 in the density of the brass weights (8·4) will produce an error of about 0·0017 grm., that is, 0·00017 per cent.

[2] W. Schlösser, *Zeit. angew. Chem.*, 16, 953, 977, 1904, 1903; N. S. Osborne and B. H. Veazey, *Bull. Bur. Standards*, 4, 553, 1908; T. Milobendzki, *Zeit. anal. Chem.*, 46, 20, 1907; G. Jones and R. E. Stanffer, *Journ. Amer. Chem. Soc.*, 59 1630, 1937. G. G. Povarnin (*Journ. Russ. Phys. Chem. Soc.*, 46, 1898, 1914) coats the inner surface of volumetric apparatus with a layer of pure paraffin to avoid adherence of drops of liquid to the surface of the glass; it also lessens the attack of alkali solutions on glass. It cannot be used for iodine or alcoholic alkali solutions.

[3] H. von Jüptner (*Chem. Ztg.*, 8, 1766, 1885) recommends three minutes' drainage for alcohol and water. See also T. Milobendzki, *Zeit. anal. Chem.* 46, 20, 1907.

The amount of liquid which adheres to the walls of a burette or other vessel is dependent upon (1) the viscosity of the liquid; (2) the adhesion of the liquid to the walls of the vessel; which in turn depends partly upon (3) the cleanliness of the walls; (4) on the surface exposed to the liquid; (5) on the rate of outflow from the jet of the burette [1] or pipette.

In illustration, contrast alcohol with concentrated sulphuric acid. Again, a pipette which delivered 100 c.c. of water at 15·5° after draining for 10 seconds, and then touching the surface of the delivered liquid with the point of the pipette,[2] delivered the volumes indicated in the accompanying Table VII. when the solutions indicated were used in place of water:—

Table VII.--Effect of the Nature of the Liquid on the Volume Delivered by a Pipette.

Solution.	Specific gravity.	Volume delivered.
Zinc sulphate	1·4246	99·52
Ammonium sulphate	1·2500	99·73
Sodium chloride	1·2072	99·75
Potassium chloride	1·1812	99·82
Ammonium chloride	1·0724	99·95
Water	1·0000	100·00

Hence it is obvious that a pipette graduated for water delivers a sensibly different volume when applied to other liquids. Pipettes may be used interchangeably for solutions not exceeding normal concentration provided the time of outflow be the same as that allowed for pure water. But a pipette or burette delivering a volume of liquid which differs appreciably in density from water requires a special calibration with that particular liquid in place of water.

According to Schlösser,[3] the effect of temperature on the drainage is negligibly small between 15° and 30°.

§ 17. The Calibration of Pipettes.

It is generally cheaper to purchase ungraduated pipettes and mark them according to the following scheme.[4] First thoroughly clean the pipette as indicated in footnote 4 on page 29. Fasten a narrow strip of paper longitudinally to the upper part of the tube. Tare a small beaker of water on the balance and suck water from the beaker into the pipette until the beaker has lost the necessary amount of water for the capacity of the pipette. Mark the position of the lower level of the meniscus with a lead pencil on the paper strip. Run the liquid into a weighed stoppered flask. Hold the pipette vertically during the outflow and let it drain 15 seconds. Remove the suspended drop by contact with a wet surface (side of flask) and include it with the delivered

[1] J. Mulder, *Die Silberprobirmethode*, Leipzig, 1859.

[2] R. R. Tatlock, *Chem. News*, **23**, 14, 1871; A. Schulze, *Zeit. anal. Chem.*, **21**, 167, 1882; W. Schlösser and C. Grimm, *Chem. Ztg.*, **30**, 1071, 1906.

[3] W. Schlösser, *Zeit. anal. Chem.*, **46**, 392, 1907; W. Schlösser and C. Grimm, *Chem. Ztg.*, **30**, 1071, 1906.

[4] F. Clowes, *Journ. Soc. Chem. Ind.*, **11**, 327, 1892. For the graduation of glass vessels, C. Foord, *Chem. News*, **30**, 191, 1874; M. C. Lea, *Amer. J. Science*, (2), **42**, 373, 1866; R. Bunsen, *Gasometrische Methoden*, Braunschweig, 28, 1877.

amount.[1] Weigh the flask and its contents. If the amount of liquid delivered from the pipette be too large, or too small, mark the paper below or above the first mark, and repeat the filling and weighing until finally the weight of liquid discharged from the pipette is exactly the amount desired at the stated temperature. The pipette may be marked with a writing diamond, the paper removed and the pipette marked all round with the diamond, or the mark may be etched with hydrofluoric acid. Now verify the accuracy of the graduation by filling the pipette as before.[2]

The "error" in pipettes allowed by testing stations is usually as follows:—

Capacity				1 to 2	10	25	50	100	200	c.c.
Permitted error				0·01	0·02	0·03	0·05		0·1	c.c.

It is easy to buy pipettes far more accurate than this.

§ 18. The Calibration of Burettes.

The burette is a most important instrument used in volumetric analysis. Burettes can be purchased accurate to 0·02 c.c. A bad burette is a nuisance, and is best discarded. To calibrate a burette, fill the burette with distilled water at the normal temperature, and withdraw successive portions ranging from 2 to 5 c.c. into a tared flask. By weighing these quantities—accurate to a milligram—the volume delivered by the burette between any two divisions can be readily determined. If a number of burettes have to be calibrated, the following procedure, based upon Scheibler's and Ostwald's methods,[3] is sufficiently exact, and it will save time.

A glass pipette is cut from an old pipette (about 2 c.c.) and mounted with the burette to be tested by means of pressure tubing and a two-way tap, as shown in the diagram, fig. 12. Two marks, a and b, respectively below and above the bulb, are cut or etched on the stem of the pipette. The pipette and the burette are thoroughly cleaned. After assembling, take care that the tubes are quite vertical. The burette, the tube between the burette and the tap and the jet of the tap are filled with pure water. Water is run into the pipette from the burette until the lower level of the meniscus is in the same horizontal plane as the lower mark of the pipette. The burette is

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[1] EMPTYING PIPETTES.—Pipettes may be emptied in at least four ways: (1) the liquid is allowed to run from the pipette without touching the pipette against the sides of the vessel; (2) by blowing out the last drop (Ostwald)—this method is useful in dealing with capillary pipettes; (3) by touching the point of the pipette against the surface of the solution; and (4) by touching the point of the pipette against the side of the vessel (a) all the time the pipette is emptying, (b) at the end of the discharge (Fresenius; Treadwell). The same method of work must be employed when the pipette is in use as is employed during standardisation. H. Göckel, Chem. Ztg., 25, 1084, 1901; 26, 159, 1902; Zeit. angew. Chem., 15, 707, 1902; 16, 49, 562, 1903; W. Schlösser, ib., 16, 977, 1903; L. A. Fischer, Journ. Amer. Chem. Soc., 20, 912, 1898; N. S. Osborne and B. H. Veazey, Bull. Bur. Standards, 4, 553, 1908.

[2] C. B. Williams, Journ. Amer. Chem. Soc., 24, 246, 1902.

[3] C. Scheibler, Journ. prakt. Chem., (1), 76, 177, 1859; W. Ostwald, ib., (2), 25, 453, 1882; W. Ostwald and R. Luther, Ausführung physiko-chemischer Messungen, Leipzig, 87, 1894; T. W. Richards, Journ. Amer. Chem. Soc., 22, 144, 1900; H. N. Morse and T. L. Blalock, Amer. Chem. Journ., 16, 479, 1894; D. W. Horn and E. M. van Wagener, ib., 30, 196, 1903; O. von Spindler, Schweiz. Woch. Chem. Pharm., 46, 145, 1908; L. W. Andrews, ib., 28, 491, 1902; D. W. Horn and E. M. van Wagener, ib., 30, 96, 1903; H. L. Payne, Journ. Anal. App. Chem., 6, 326, 1892; M. J. C. Boot, Rec. Trav. Pays-Bas., 13, 417, 1894; D. Carnegie, Chem. News, 64, 42, 1891. W. Ostwald (l.c.) and A. S. Cushman (Journ. Amer. Chem. Soc., 23, 482, 1901) use a pipette with the upper stem graduated. The error is read directly on the graduated stem of the pipette every time the pipette is filled with, say, 2 c.c. of liquid from the burette. This pipette is easily obtained by using one of Cobbett's pipettes instead of that indicated in the text. For calibrations with mercury, C. A. Bell, Proc. Chem. Soc., 17, 179, 1901; Chem. News, 83, 21, 1901.

filled to zero. Water is run from the burette until the pipette is filled to the mark b. Read the burette. This water is then discharged from the pipette. The filling and emptying of the pipette is continued until insufficient water remains in the graduated portion of the burette to fill the pipette. The
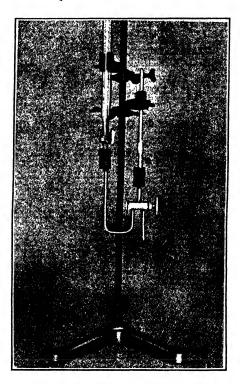
FIG. 12.—Calibration of a Burette.

burette is read each time the pipette is filled. Two minutes are allowed for drainage, as indicated above.

Suppose that the 50 c.c. burette has filled the pipette 16 times, and, as a mean of three comparisons, the burette reads 49·64 c.c. The burette is then refilled, and exactly the same amount of water is run from the burette into a weighed flask. The weight of water gives the necessary data for calculating the volume of the pipette. Suppose we get a weight of 49·64 grms. at 18·5°. From the table, page 22, we see that the density of water at this temperature is 0·9985, and its volume is therefore 49·64 ÷ 0·9985 = 49·71 c.c. Hence,
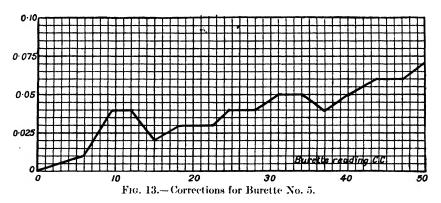
$$\text{Volume of water in pipette } (18\cdot5°) = \frac{49\cdot71}{16} = 3\cdot107 \text{ c.c.}$$

Suppose that the numbers in the second column of Table VIII. represent the successive readings of the burette under the conditions just indicated. The numbers in the third column of Table VIII. will represent the corresponding volumes, that is, the product of 3·107 with the corresponding number in the first column. The fourth column gives the error of the readings indicated in the second column.

Table VIII.—Burette Corrections—Burette No. 5.

Number of reading.	Burette reading.	Corrected burette reading.	Corrections.
	c.c.	c.c.	c.c.
1	3·11	3·11	0·00
2	6·20	6·21	+0·01
3	9·28	9·32	+0·04
4	12·39	12·43	+0·04
5	15·51	15·53	+0·02
6	18·61	18·64	+0·03
7	21·72	21·75	+0·03
8	24·53	24·57	+0·04
9	27·92	27·96	+0·04
10	31·02	31·07	+0·05
11	34·13	34·18	+0·05
12	37·24	37·28	+0·04
13	40·34	40·39	+0·05
14	43·44	43·50	+0·06
15	46·54	46·60	+0·06
16	49·64	49·71	+0·07

These numbers can be plotted on squared paper (fig. 13): ordinates, corrections (Column 4); abscissæ, readings (Column 2). Hence the correction

FIG. 13.—Corrections for Burette No. 5.

for any reading of the burette can be seen at a glance. In the present example, the burette reads 49·64 when the corresponding volume is 49·71 c.c. Hence that burette reading is to be corrected by +0·07 c.c. Had the corrected reading for another burette been 49·59 c.c., the actual burette reading 49·64 c.c. would have been corrected by −0·05 c.c. The sign of the correction wants thinking over. This burette is unsatisfactory—probably the bore of the tube is not uniform.

The following "errors" are usually "permitted" at a standard testing station:—

Capacity	.	.	.	1 to 2	2 to 10	10 to 30	30 to 50	50 to 100 c.c.
Permitted error	.	.	.	0·01	0·02	0·03	0·05	0·10 c.c.

For parts of the volume less than half the total content, the limits of error are one-half the above.

The burette nozzle should be such that the time of delivery of the burette does not exceed 100 seconds.   Wagner (*l.c.*) thinks that 70 seconds is sufficient for the time of outflow.[1]   It might also be added that Förster [2] noticed that burettes which have been used with alkaline solutions increase perceptibly in volume.   Thus, one is mentioned which changed from 50 c.c. to 51 c.c. after being in use for a year.   Such burettes must be frequently calibrated.[3]

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[1] LUBRICANTS FOR GLASS STOPCOCKS.—F. C. Phillips, *Journ. Amer. Chem. Soc.*, **20**, 149, 1898; *Chem. News*, **78**, 311, 1898.   According to L. L. de Koninck and M. Lejeune (*Bull. Soc. Chim. Belg.*, **23**, 79, 1909) stopcock burettes for iodine and permanganate solutions may be safely greased with vaseline.

[2] O. Förster, *Chem. Ztg.*, **28**, 147, 1904.

[3] For general reports on volumetric apparatus, see *Mitt. der K.N.E.K.*, **3**, 5, 1908; *Internat. Kong. angew. Chem.*, **7**, 41, 1909.

CHAPTER III.

VOLUMETRIC ANALYSIS.

§ 19. Normal Solutions.

In volumetric analysis [1] a standard solution of known strength is gradually added to a solution of the substance under investigation until the reaction between the two is completed. The volume of the standard solution required for this purpose is proportional to the amount of the substance in the solution under investigation. The two solutions must be of such a kind that the reaction takes place quickly and quantitatively. It must also be possible to recognise the end of the reaction. This is frequently indicated by a change in colour which occurs in the presence of a third substance, the **indicator**, immediately a small excess of the standard solution has been added. [2] The indicator is usually indifferent to the main reaction. Since a definite amount of the standard solution can react with a definite amount of the substance under investigation, given the volume of the standard solution, the amount of the substance under investigation can be calculated by simple proportion.

The standard solutions may be of any strength, but it is convenient to make them of such a strength that the weight of the dissolved substance, per litre, bears a simple numerical relation to the molecular weight of the compound. *A solution which contains the hydrogen equivalent weight in grams of an element or compound per litre is called the* **normal solution**, written N-solution; a semi-normal solution is one-half the strength of a normal solution—0·5 N-solution; a decinormal solution—0·1 N-solution—is one-tenth the strength of a normal solution; and a centinormal solution—0·01 N-solution—is one-hundredth the strength of a normal solution.

The "equivalent weight" of a substance is the number of grams of the substance which brings into reaction—combination or replacement—the equivalent of 1·008 grms. of hydrogen [3] or 8 grms. of oxygen. To illustrate further, the molecular and equivalent weights of HCl, $NaOH$, $NaCl$, $AgNO_3$, NH_4CNS and $Na_2S_2O_3.5H_2O$ are identical; the equivalent weights of $H_2C_2O_4$, H_2SO_4, $Ba(OH)_2$ and $CaCO_3$ are half the molecular weights; the equivalent weight of As_2O_3 is one-fourth the molecular weight; the equivalent weight of $KMnO_4$ in acid solution is one-fifth the molecular weight; and the equivalent weights of KIO_3 and $K_2Cr_2O_7$ are one-sixth the molecular weights.

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[1] Following up some early suggestions by E. A. H. Descroizilles (1802) and L. N. Vauquelin (1812), J. L. Gay-Lussac demonstrated the applicability and utility of volumetric methods in analytical chemistry—for chlorimetry, 1824; for alkalimetry, 1828; silver, 1832. See L. L. de Koninck, *Bull. Assoc. Belg. Chim.*, **19**, 28, 73, 422, 1904; *Chem. News*, **84**, 207, 1901; *Histoire de la Methode Titrimétrique*, Brussels, 1901; H. Beckurts, *Die Methoden der Mass-analyse*, Braunschweig, 1031, 1913.

[2] H. Lescoeur, *Compt. rend.*, **123**, 811, 1896; *Chem. News*, **74**, 285, 1896.

[3] The exact value is 1·0081, but all calculations in this work have been based on the rounded-off figure of 1·008.

It is not always easy to see how the equivalent weight of some of these substances is determined, hence a few illustrations may be cited. In titrating iodine solutions with sodium thiosulphate, the reaction is represented by the symbols: $2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$. Here one molecule of sodium thiosulphate is equivalent to one atom of iodine, which, in turn, is equivalent to one atom of hydrogen. Hence the equivalent of $Na_2S_2O_3.5H_2O$ is numerically equal to the molecular weight.

With potassium dichromate, in titrating ferrous salts, we have the reaction: $K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$. This reduces to $3O + 6FeO = 3Fe_2O_3$. Hence the potassium dichromate furnishes three atoms of oxygen, which, in turn, correspond with six atoms of hydrogen. Hence the molecule of potassium dichromate is equivalent to six atoms of hydrogen, or the equivalent is one-sixth the molecular weight.

The case of potassium permanganate is a little curious. When ferrous sulphate is oxidised by potassium permanganate in acid solution, the equation

$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

reduces to

$$5O + 10FeO = 5Fe_2O_3$$

Or, two molecules of potassium permanganate furnish five atoms of oxygen, which are equivalent to ten atoms of hydrogen. Hence the normal solution of $KMnO_4$ will contain one-fifth of the molecular weight, that is $\frac{1}{5}$ of $2 \times 158 \cdot 026 = 31 \cdot 6052$ grms. per litre. In Volhard's process for manganese, the titration is made in neutral solution. The reaction is

$$2KMnO_4 + 3MnSO_4 + 2ZnO = 5MnO_2 + K_2SO_4 + 2ZnSO_4$$

which reduces to

$$Mn_2O_7 + 3MnO = 5MnO_2$$

Or, two molecules of potassium permanganate give three atoms of oxygen, so that the normal solution contains $\frac{1}{6}$ of $2 \times 158 \cdot 026 = 52 \cdot 6753$ grms. per litre, or the equivalent weight is one-third the molecular weight. Hence there are two different normal solutions, depending on the particular reaction under consideration. But potassium permanganate is generally used in acid solution and in consequence, unless otherwise expressed, a normal solution of potassium permanganate is understood to contain $31 \cdot 6052$ grms. per litre.[1]

Again, in titrating stannous chloride with ferric chloride, two molecules of the latter give two atoms of chlorine to one molecule of stannous chloride:

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$$

Hence one molecule of ferric chloride is equivalent to one atom of chlorine, which, in turn, is equivalent to one atom of hydrogen. The molecular and equivalent weights are identical. A normal solution of stannous chloride, on the other hand, will have half the molecular weight of $SnCl_2$ expressed in grams per litre, because one molecule of stannous chloride takes two atoms of chlorine from two molecules of ferric chloride.

The preceding definition of normal solutions is virtually that given by F. Mohr in 1859.[2] This definition has been adopted by the leading writers on

[1] For "the available oxygen" standard, see R. Abegg, *Anleitung zur Berechnung volumetrischer Analysen*, Breslau, 1900.

[2] F. Mohr, *Lehrbuch der chemisch-analytischen Titriermethode*, Braunschweig, 1859; W. Fresenius, *Zeit. anal. Chem.*, **25**, 205, 1886; B. Tollens, *ib.*, **25**, 363, 1886; C. Marx, *ib.*, **26**, 217, 1887; L. L. de Koninck, *ib.*, **25**, 487, 1886; A. H. Allen, *Chem. News*, **40**, 239, 1887; C. Winkler, *Die Massanalyse nach neuen titrimetrischen System*, Freiburg, 1883; *Ber.*, **18**, 2527, 1885; *Zeit. anal. Chem.*, **25**, 484, 1886.

volumetric analysis (C. R. Fresenius, F. Sutton, E. F. Fischer, A. Classen), and most analysts. Other definitions have been proposed, and a few writers (N. Menschutkin, M. M. P. Muir, C. Winkler, J. Muter) have defined a normal solution to be a "solution containing the molecular weight of the salt in grams per litre." This definition is advantageously used in physical chemistry, but not in analytical chemistry. It might be noted *en passant* that Gay-Lussac's "normal solution of sodium chloride" is "a solution of sodium chloride such that 100 c.c. will exactly precipitate 1 gram of silver." This special definition is used in many assaying laboratories for these particular solutions.

§ 20. Standard Solutions of Hydrochloric Acid.

Hydrochloric acid— HCl. Molecular weight: 36·465; equivalent weight: 36·465.

The most commonly used solutions are:—

	Grm. HCl per c.c.
N-Hydrochloric acid	0·036465
0·5N-Hydrochloric acid	0·018232
0·2N-Hydrochloric acid	0·007293
0·1N-Hydrochloric acid	0·003646

To prepare a seminormal solution of hydrochloric acid, that is, a solution of hydrochloric acid containing half the equivalent weight (*viz.* 18·2325 grms.) per litre, make a solution rather more concentrated than is finally needed; determine the exact strength by comparison with another solution of known titre, or by analysis; and then dilute to the required strength.

Suppose the hydrometer shows that the stock of concentrated acid has a specific gravity 1·14. From gravity tables, an acid of this strength contains at 15° 315 grms. of HCl per litre. Hence, 68 c.c. of this acid will have between 21 and 22 grms. of HCl. Make 68 c.c. of this acid up to 1100 c.c. in a Giles' flask [1] with recently boiled distilled water. Let the solution stand a few hours so that it may attain the temperature of the room. If the temperature of the room be not that given on the flask, an allowance must be made as indicated in Table V., IX. or XI.

Compact fragments of Iceland spar [2]—calcium carbonate—weighing from 2 to 3 grms. each, are broken from a large crystal by pressing the edge of the blade of a knife against a large clear crystal and tapping the back of the blade sharply with a hammer. These fragments are rinsed with dilute hydrochloric acid or nitric acid to free them from adhering powder and to round their edges and corners. They are then well washed with distilled water and dried in an oven at 110°. The pieces are preserved in a stoppered bottle for use.

Two or three pieces of the Iceland spar are placed in a clean dry beaker or

[1] W. B. Giles, *Chem. News*, 69, 99, 1894; W. Wislicenus, *Ber.*, 29, 2442, 1896.
[2] Selected crystals are remarkably pure—purer, indeed, than the regular "sodium carbonate purissimus" normally used for standardising hydrochloric acid. This excellent method of standardising hydrochloric acid was recommended by G. Duerr, *Chem. News*, 28, 156, 1873; O. Masson, *ib.*, 81, 73, 1900; W. H. Green, *ib.*, 87, 5, 1903; H. Thiele and R. Richter, *Zeit. angew. Chem.*, 13, 486, 1900. See J. W. Young, *Can. Chem. Met.*, 18, 218, 1934; G. A. Hulett and W. D. Bonner, *Journ. Amer. Chem. Soc.*, 31, 390, 1909; J. A. Shaw, *Ind. Eng. Chem.*, 18, 1065, 1926; L. W. Andrews, *Journ. Amer. Chem. Soc.*, 36, 2089, 1914; C. T. Moody, *Journ. Chem. Soc.*, 73, 658, 1898; C. L. Higgins, *Journ. Soc. Chem. Ind.*, 19, 958, 1900, for alternative methods of standardisation. See L. Vanino and E. Seitter (*Zeit. anal. Chem.*, 41, 141, 1902) for a review of processes and materials for preparing standard solutions. Compare E. Hinks, *Analyst*, 55, 238, 1930; J. Grant, *Chem. and Ind.*, 76, 1934; O. Johnson, *Ind. Eng. Chem. Anal. Ed.*, 7, 76, 1935.

Erlenmeyer's flask. Weigh the beaker and contents, all dried at 110° and cooled in a desiccator. Cover the beaker with a watch-glass and add 20 c.c. of the hydrochloric acid from the flask [1] by means of a clean pipette in such a way that there is no loss by spurting. When the evolution of gas has almost ceased (3–4 hours) rinse the side of the beaker with distilled water. Replace the cover and heat the solution to near the boiling-point on an asbestos pad or silica plate for about an hour. This is to ensure that the reaction between the acid and the spar is complete. Bumping must not be permitted, or minute fragments may be detached from the undissolved spar, which would cause high results. Decant off the solution, wash the beaker and the residual spar thoroughly with distilled water, dry the beaker and contents at 110°, cool in a dessicator and weigh. This gives the data necessary for calculating the strength of the acid. For example:

First weight of beaker and spar	21·6327 grms.
Second weight of beaker and spar	21·1016 grms.
Iceland spar dissolved	0·5311 grm.

Since the molecular weight of Iceland spar is 100 (more exactly 100·08), and

$$2HCl + CaCO_3 = CaCl_2 + H_2O + CO_2$$

it follows that 2 litres of normal acid will dissolve 100 grms. of the Iceland spar, or 20 c.c. will dissolve 1 gram. Had the acid been exactly half-normal, 0·5 grm. of the spar would have dissolved.[2] The acid we have prepared is too concentrated. Pipette acid from the Giles' flask until the level of the liquid is at the 1000 c.c. mark. Since 0·5311 grm. of Iceland spar is dissolved by 20 c.c. of the acid solution, 0·5 grm. will be dissolved by $0·5 \times 20/0·5311 = 18·83$ c.c. of this solution. Thus, in order to make the acid exactly half-normal, 18·83 c.c. must be diluted with 1·17 c.c. of water. Hence, the 1000 c.c. now in the Giles' flask must be diluted with 62·1 c.c. of water in order to make the solution exactly half-normal. The accuracy of the dilution should be established by repeating the experiment with the Iceland spar.[3] The most important source of error in this method of standardising the hydrochloric acid arises from the fact that the reaction is somewhat tardy towards the end, hence sufficient time must be allowed for the completion of the reaction between the acid and spar.

Numerous substances, other than Iceland spar, have been proposed and used for the standardisation of acids.[4]

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[1] If ordinary flasks are used the volume withdrawn for testing, etc., should be noted, so as to avoid the use of measuring cylinders later on when the solution is diluted.

[2] It is here assumed that 100 is the molecular weight of the Iceland spar. If 100·08 be taken, the corresponding change must be made in the other numbers.

[3] It should be remembered that in diluting the more concentrated solutions, a change of volume may occur such that the volume of the mixture is less or greater than the sum of the separate volumes of the two components. The effect is seldom appreciable with dilute solutions, but with more concentrated solutions the effect may be serious if the dilution be not checked. Thus, with a solution of ammonium sulphate containing 56 grms. per 100 c.c., the contraction was found to be:

Ammonium sulphate solution taken . . .	50·0	25·0	12·5 c.c.
Water taken	50·0	75·0	87·5 c.c.
Volume of resulting solution	98·83	99·64	99·89 c.c.

Changes of temperature on mixing sometimes cause a temporary expansion. Sufficient time must be allowed for the mixture to assume the temperature of the room before measuring the liquid or the control experiment.

[4] For example, sodium carbonate, M. Randall and C. C. Scalione, *Met. Chem. Eng.*, **13**, 707, 1915; W. Worms, *Journ. Russ. Phys. Chem. Soc.*, **28**, 432, 1897; J. Linder and N. Figala, *Zeit. anal. Chem.*, **91**, 105, 1932; L. Waldbauer, D. C. McCann and L. F. Tuleen, *Ind. Eng. Chem. Anal. Ed.*, **6**, 336, 1934; G. F. Smith and G. F. Croad, *ib.*, **9**, 141, 1937;

The advantages of hydrochloric acid as the standard acid for general work are: (1) it forms readily soluble salts with the alkalies and the alkaline earths (hence preferable to sulphuric and oxalic acids); (2) it is easily obtained pure (nitric acid often contains a little nitrous acid); (3) the strength of the acid is easily verified by means of silver nitrate; (4) the dilute solutions used suffer no perceptible loss of acid when boiled for instance, a 0·2N-solution boiled 10 minutes did not redden blue litmus paper held in the vapour, hence the steam which passes off is almost free from hydrochloric acid; (5) the strength of the acid does not change on keeping.[1]

§ 21. Temperature Correction for Solutions of Hydrochloric Acid.

It has been assumed that the temperature of the acid solution did not differ more than 3° from the standard temperature, 15°. If the actual temperature deviates appreciably from this number, a correction must be applied in order to obtain the strength of the acid at the standard temperature. The following correction table Table IX. is to be used in accurate work when using a normal solution of hydrochloric acid at a temperature different from that at which it was standardised, namely, 15°.[2] For solutions more dilute than one-tenth normal the correction table, page 22, for water may be used.

Table IX. Temperature Correction for N-HCl Solutions.
(Standard temperature, 15°. Corrections in c.mm. per c.c.)

Temp.	0	1	2	3	4	5	6	7	8	9
0	..	..	..	..	..	+1·3	+1·2	+1·1	+1·0	+0·9
10	+0·8	+0·7	+0·5	+0·3	+0·2	Zero	-0·2	-0·4	-0·6	-0·8
20	-1·1	-1·3	-1·5	1·8	-2·1	-2·3	2·5	2·8	3·1	-3·4

EXAMPLES.—(1) 21·30 c.c. of 1·0N-HCl have been used in a titration at 22°. The solution was standardised for 15°. The actual volume at 15° would be less than 21·30 c.c. From Table IX. the correction for 1 c.c. is 0·0015 c.c. Hence, 21·3 × 0·0015 = 0·032 c.c. or 21·30 c.c. at 22° correspond with 21·30 − 0·03 = 21·27 c.c. at 15°.

potassium bicarbonate, L. W. Winkler, *Zeit. angew. Chem.*, 28, 264, 1915; C. Ineze, *Zeit. anal. Chem.*, 54, 585, 1915; G. Bruhns, *Chem. Ztg.*, 48, 89, 1924; thallous carbonate, R. Hac and K. Kamen, *Czechoslov. Chem. Comm.*, 4, 145, 1932; *Chem. Listy*, 26, 6, 1932; guanidine carbonate, A. H. Dodd, *Journ. Soc. Chem. Ind.*, 40, 89T, 1921; diphenylguanidine, C. A. Carlton, *Journ. Amer. Chem. Soc.*, 44, 1851, 1922; borax, W. Worms, *l.c.*; M. G. Mellon and V. M. Morris, *Ind. Eng. Chem.*, 17, 145, 1925; F. H. Hurley, junr., *ib. Anal. Ed.*, 8, 220, 1936; 9, 237, 1937; I. M. Kolthoff, *Journ. Amer. Chem. Soc.*, 48, 1447, 1926.

[1] Among other substances which have been proposed as acidimetric standards are: oxalic acid, W. Worms, *l.c.*; C. M. van der Feen, *Chem. Weekb.*, 12, 1021, 1915; A. Blanchetière, *Bull. Soc. chim.*, (4), 19, 300, 1916; potassium tetroxalate, F. T. B. Dupré and A. von Kupffer, *Zeit. angew. Chem.*, 15, 352, 1902; adipic acid, F. T. van Voorst, *Chem. Weekb.*, 25, 22, 1928; salicylic acid, J. Rosický and J. Tamchyna, *Chem. Listy*, 25, 468, 1931; picric acid, O. Pfeiffer, *Zeit. angew. Chem.*, 27, 383, 1914; benzoic acid, S. V. Lipin, Z. E. Lukina and S. A. Konovalova, *Trav. inst. métrol. standard. U.S.S.R.*, 6, 59, (68), 1934; alkali phthalates, W. S. Hendrixson, *Journ. Amer. Chem. Soc.*, 42, 724, 1655, 1920; 37, 2352, 1915; F. D. Dodge, *Ind. Eng. Chem.*, 7, 29, 1915; sulphuric acid (indirect methods), C. A. Kohn, *Journ. Soc. Chem. Ind.*, 19, 962, 1900; H. B. van Valkenburgh, *Journ. Amer. Chem. Soc.*, 42, 757, 1920; arsenious oxide, A. W. C. Menzies and F. N. McCarthy, *Journ. Amer. Chem. Soc.*, 37, 2021, 1915.

[2] The table also applies for N-oxalic acid. It is based on A. Schulze (*Zeit. anal. Chem.*, 21, 167, 1882). The table can be readily transposed into any other standard temperature different from 15°, as indicated on page 22. For tables of corrections, see also Y. Osaka, *Journ. Tokyo Chem. Soc.*, 32, 450, 1911; 40, 424, 1919; *Journ. Chem. Soc.*, 118, (2), 187, 1920.

(2) A titration is made at 12°, and later on at 20°. In the former case, 19·99 c.c. were used, and in the latter case, 20·02 c.c. Suppose that no temperature correction be made, it follows that the two determinations give a difference of 100(20·02 – 19·99) ÷ 19·99 · 0·15 per cent. As a matter of fact, both really correspond with 20 c.c. at the standard temperature, 15°.

These two examples give an idea of the error to which we are liable when the temperature is neglected. The temperature factors will be given for other solutions as occasion demands.

In order to facilitate the preparation of standard solutions at temperatures different from the standard, Heygendorff[1] has designed measuring flasks graduated for, say, 1000 c.c. at temperatures between 9° and 25°.[2]

§ 22. The Adjustment of Standard Solutions.

When large volumes of a solution are in question, the adjustment can be made without measuring the volume of the liquid litre by litre.[3] Suppose that 40 50 litres of a 0·1N-soda solution are to be prepared. Nearly fill the storage carboy with a solution, say, 25 per cent. over-strength. Pipette, say, three lots of 25 c.c. and titrate with 0·1N-acid as indicated later on. Suppose that 25 c.c., as a mean of three titrations, require 31·25 c.c. of the standard acid. In that case, 80 c.c. of the given solution correspond with 100 c.c. of the 0·1N-acid. This means that 250 c.c. of water must be added per litre of the solution in order to make it exactly 0·1N. Now transfer, say, 200 c.c. of the solution into a 500 c.c. flask.

Add a litre of water to the solution: stir; withdraw, say, 200 c.c. for titration. Suppose that 83·33 c.c. now correspond with 100 c.c. of the 0·1N-acid and 200 c.c. of water must be added per litre of the solution in order to make it exactly 0·1N. Thus on the addition of a litre of water to the stock solution, the volume of water needed to dilute each litre of the stock solution down to 0·1N strength is reduced by 50 c.c. Hence to produce a total reduction of 250 c.c., 250/50 = 5 litres will be needed. But as 1 litre has been added, 4 more litres of water must be added.

A slight error is caused by withdrawing 200 c.c. for the second trial. To correct this, dilute the 200 c.c. of the stock solution standing in the 500 c.c. flask by adding 50 c.c. of water per litre; that is, 200 c.c. require 10 c.c. of water. The solution in the flask is now the same strength as the 200 c.c. withdrawn for the second titration before adding the 4 litres of water. Hence, add 200 c.c. of the stock solution, diluted as indicated above, to the liquid in the carboy, and, if there has been no change of volume on mixing, the solution should be exactly decinormal, and occupy 25 litres.

Some prefer to leave the acid approximately 0·5N, instead of adjusting the solution exactly, as described on page 39, by means of the Giles' flask. In that case, 20 c.c. of the acid are equivalent to 0·5311 grm. of calcium carbonate. But, from the above equation, 100 grms. of Iceland spar correspond with 72·93 grms. of hydrochloric acid, and therefore 0·5311 grm. of Iceland spar will correspond with 0·7293 × 0·5311 = 0·3873 grm. HCl. Hence, 20 c.c. of the acid has 0·3873 grm. HCl; or 1 c.c. has 0·019365 grm. HCl. The bottle containing the solution may be labelled accordingly.

If but a small volume of acid is to be standardised, it may be advisable to

[1] M. von Heygendorff, *Chem. Ztg.*, 35, 382, 1911.
[2] For charts, see H. C. Deming, *Ind. Eng. Chem.*, 8, 271, 451, 1916.
[3] F. M. Lyte, *Chem. News*, 26, 159, 1872; 29, 23, 1874; W. Smith, *ib.*, 20, 220, 1869. Compare E. J. Leeming, *School Sci. Rev.*, 16, 416, 1935.

follow the plan just described. In other cases a factor may be used. In the above example, the acid has 0·3873 grm. HCl per 20 c.c. If it were exactly half-normal, 20 c.c. would have 0·36465 grm. HCl. Or 18·83 c.c. are equivalent to 20 c.c. of half-normal acid; or the acid is 0·5311N when it should be 0·5N. Dividing any pair of these numbers, say,

$$\frac{0·5}{0·5311} = 0·9415$$

the resulting number—0·9415—represents the fraction of a cubic centimetre which is equivalent to 1 cubic centimetre of exactly 0·5N-acid. Hence, in any given titration, the number of cubic centimetres divided by 0·9415 will give the number of cubic centimetres which would have been used with exactly 0·5N-acid. Similarly, had 0·4311 grm. of spar been dissolved, the acid would have been too dilute, and the conversion factor would have been 0·5 ÷ 0·4311 = 1·16.[1]

§ 23. The Adjustment of the Specific Gravity of Solutions.

Solutions of a definite specific gravity have sometimes to be made by diluting solutions of known specific gravity. Usually very great accuracy in dilution is not needed.[2] When tables connecting specific gravity with concentration are available, the method can also be applied to the dilution of solutions of a given percentage composition to solutions of another percentage composition. In the absence of a knowledge of the law of contraction or expansion on dilution, the problem can only be solved approximately, because the methods of calculation assume that "the total volume of a mixture is equal to the sum of the volumes of its parts," and this assumption is not always justified. The following represent three typical cases:—

1. *It is required to prepare a volume* V *of a solution of specific gravity* S, *by diluting a volume* v *of a solution whose specific gravity is* s. Here V, S and s are known, v is to be determined. It follows that $V - v$ will be the volume of the water needed, and we must have $vs + V - v = VS$. Hence, it follows

$$v = \frac{V(S-1)}{s-1} \qquad . \qquad . \qquad . \qquad . \qquad . \quad (1)$$

EXAMPLE.—Soda lye of specific gravity 1·34 is to be diluted with water to make 50 c.c. of a solution of specific gravity 1·11. How much soda lye must be taken? Here, $V = 50$, $S = 1·11$, and $s = 1·34$, hence $v = 16·18$ c.c.

2. *It is required to dilute a volume* v *of a solution of specific gravity* s, *so as to make a solution of specific gravity* S—*to find the amount of water needed.* Here

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[1] M. E. Pozzi-Escot, *Bull. Assoc. Chim. Sucr. Dist.*, **31**, 124, 1913; E. Petersen (*Zeit. anal Chem.*, **45**, 14, 439, 1906; G. Bruhns, *ib.*, **45**, 204, 1906) recommends the adjustment of standard solutions by representing the approximately normal solution in terms of "equivalent volumes" —that is, the number of cubic centimetres of the solutions which contain an equivalent weight of the substance in solution. Thus, in standardising hydrochloric acid, we have found 0·5311 grm. of Iceland spar to be equivalent to 20 c.c. of acid; hence, half of one equivalent of Iceland spar, namely, 25 grms., would be equivalent to half an equivalent of hydrochloric acid, and equivalent to 941·5 c.c. of the solution. Hence, the equivalent volume of the solution was 941·5 c.c.

[2] A. Vogel, *Deut. Illustr. Gewerbezeit.*, 202, 1865; C. D. Howard, *Journ. Amer. Chem. Soc.*, **19**, 587, 1897; *Ind. Eng. Chem.*, **7**, 807, 1915; P. F. Bovard, *ib.*, **7**, 358, 1915; G. Surr, *Min. Eng. World*, **39**, 1075, 1913; A. Cobenzl, *Farben Ztg.*, **21**, 1277, 1916. See almost any text-book on the elements of hydrostatics.

v, s and S are known—to find V. When V has been determined, the required volume is given by $V - v$. From the preceding relation, we see that

$$V - v = \frac{v(s - S)}{S - 1} \qquad . \qquad . \qquad . \qquad . \qquad (2)$$

EXAMPLE.—What volume of water is needed to reduce 50 c.c. of a solution of caustic soda of specific gravity 1·34 to a specific gravity 1·11? Here, $v = 50$, $S = 1·11$, $s = 1·34$, hence $V - v = 104·55$ c.c.

3. *It is required to dilute* v *c.c. of a solution of specific gravity* s *with another liquid of specific gravity* z *in order to get a solution of specific gravity* S—*to find what volume of liquid of specific gravity* z *is necessary for the purpose.* Here v, s, z and S are known. Let u denote the required volume of the solution of specific gravity z, then

$$u = \frac{v(s - S)}{S - z} \qquad . \qquad . \qquad . \qquad . \qquad (3)$$

EXAMPLE.—50 c.c. of soda lye, specific gravity 1·34, are to be diluted with soda lye, specific gravity 1·11, in order to get a solution of specific gravity 1·2. What volume of the latter is needed? Here, $v = 50$, $z = 1·11$, $s = 1·34$, $S = 1·2$, hence $u = 77·78$ c.c.

The problem of dilution is usually very easily solved by means of the specific gravity tables.

EXAMPLE.—A solution of sulphuric acid, specific gravity 1·2, is to be prepared from the stock acid, specific gravity 1·84. From gravity tables, 100 c.c. of acid of specific gravity 1·84 has 175·9 grms. H_2SO_4, and 100 c.c. of acid of specific gravity 1·2 has 32·8 grms. H_2SO_4. If 175·9 grms. H_2SO_4 are contained in 100 c.c. of acid of specific gravity 1·84, 32·8 grms. H_2SO_4 will be contained in 18·65 c.c. of this acid. Hence, if 18·65 c.c. of the concentrated acid be transferred to a 100 c.c. flask, and the solution made up to 100 c.c. (temperature constant), the result will be an acid of the desired concentration.

§ 24. The Calculations of Analytical Chemistry.

Slide Rule.— The slide rule is a convenient check on the accuracy of the arithmetic. The regular slide rule of moderate length does not read to more than two figures and a third by approximation, that is, approximately to the first decimal of one per cent. It is customary to write two decimals, in spite of the fact that the second figure is of no real value. Chemists have not therefore taken up the slide rule, owing to the uncertainty in the third and fourth figures. It is a general principle in chemical arithmetic that *the magnitude of the error due to the method of calculation must be well within the limits of the experimental error.* The ordinary slide rule does not satisfy this criterion. Hence, the chief function of the ordinary slide rule is to check the accuracy of calculations.[1] Errors which might escape detection by simply going over the figures may be thus revealed.

Squared Paper.[2]—Let 1000 be taken as an abscissa on squared paper, and as ordinate lay off a length corresponding with the reduction factor of a given determination, say 736 for lead oxide in lead sulphate; 247 for chlorine in silver chloride. Join, say, the ordinate 736 with the abscissa zero, then any particular weight of $PbSO_4$, found by analysis, is located on the abscissa axis, and the corresponding amount of PbO is read on the ordinate axis. This method is useful for *checking calculations* and, if the curve be drawn on a

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[1] H. C. Deming, *Journ. Ind. Eng. Chem.*, 8, 271, 451, 1916; *Journ. Amer. Chem. Soc.*, 39, 2137, 2388, 1917. W. H. Wollaston (*Phil. Trans.*, 104, 1, 1814) described a slide rule very similar to some types in use to-day.

[2] F. P. Dunnington, *Journ. Amer. Chem. Soc.*, 25, 537, 1903.
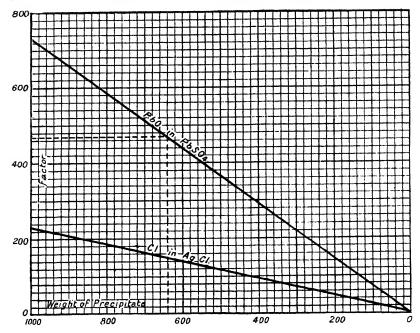
Fig. 14.—Charts to Facilitate Calculations.

larger scale, it will be found as convenient as a table for saving time in analytical calculations.

EXAMPLE.—Suppose a precipitate of lead sulphate weighs 0·64 grm. The ordinate —fig. 14 (dotted lines)—corresponding with the abscissa 0·64 is 0·47; hence 0·47 grm. is the equivalent weight of PbO corresponding with 0·64 grm. of PbSO₄.

Analytical Tables. – Logarithms are in common use. Five-figure logarithmic tables suffice for the calculations in most analytical work.[1] In order to lessen the labour involved in calculating oft-repeated determinations, conversion tables may be used with advantage. This prevents wasting time and energy on a repetition of old operations, and conduces to more accurate work. Once accurate tables have been compiled, there is less liability to error.

Rational Weighing.—Another artifice for abbreviating calculations is to weigh an amount of substance for the analysis which bears a simple relation to the conversion factor.[2] *When the amount of substance taken for analysis is the same as the conversion factor, the weight of the precipitate directly corresponds with the percentage value sought;* and when the amount of substance taken for analysis is a simple multiple or sub-multiple of the conversion factor, the weight of the precipitate is a corresponding multiple or sub-multiple of the percentage value sought. For instance, if PbO is to be determined in a given substance, and if 0·7360 grm. of the sample be taken, then, if 0·5 grm. of lead sulphate be obtained, it follows that the sample contains 50 per cent. of PbO. It is easy to see this. Since 0·5 × 0·7360 grm. of PbO has been obtained from 0·7360 grm. of the sample, 100 grms. of the sample will have 50 grms. of PbO.

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[1] For example, F. D. Küster, *Logarithmische Rechentäfeln für Chemiker*, Berlin, 1919; C. J. Woodward, *Five-figure Logarithms for Chemists*, London, 1910.

[2] E. A. Uehling, *Journ. Anal. App. Chem.*, **1**, 402, 1887. E. B. and L. A. Voorkees (*ib.*, **7**, 121, 1893) recommend specially graduated pipettes.

It must be remembered that time is lost in weighing a definite amount of a substance to such a degree of accuracy, and it is sometimes questionable if the time consumed in weighing is not greater than the time spent in solving the proportion, in this particular case:

Weight of sample : 0·7360 = Weight of lead sulphate : x

At any rate, the risk of error, owing to the hygroscopic properties of fine powders, is sometimes greater in the former case. Similarly in volumetric work, a little thought spent in "designing" routine operations may save a great deal of work.

To find the relation between the weight of the sample to be taken for the analysis and the concentration of the standard solution used so that the number of cubic centimetres of the standard solution may directly represent the percentage amount of the constituent sought. -The strength of the standard solution must be adjusted so that a weight w of the sample is equivalent to 100 c.c. In other words, 100 c.c. of the standard solution must be equivalent to a weight w of the (pure) constituent sought. For example, if 100 c.c. of the standard solution be equivalent to 3·942 grms. of the constituent under investigation, we must weigh exactly 3·942 grms. of the sample for the titration. In that case, if 41 c.c. of the standard solution be used in the titration, the sample contains 41 per cent. of the constituent in question.

EXAMPLE.—Suppose that it be required to determine the amount of sodium carbonate in a given sample of soda ash. For convenience, let $w = 1$ grm. The standard acid solution must be so made that 100 c.c. contain the equivalent of 1 grm. of sodium carbonate. By weighing 1 grm. of the sample for each determination, every c.c. of the acid used in the titration will represent 1 per cent. of sodium carbonate in the sample.

It may be advisable to use a more dilute solution. The strength of the standard solution can be made such that the percentage amount of the constituent sought in the given sample is one-tenth the number of cubic centimetres used in titration. Then, 1000 c.c. of the standard solution must be made equivalent to w grms. of the constituent (pure) under investigation.

EXAMPLE. –Suppose that it be required to find the percentage amount of sodium chloride in a sample of soda ash. For convenience, let $w = 2$. The standard solution of silver nitrate must be made such that 1000 c.c. correspond with 2 grms. of sodium chloride. But 2 grms. of sodium chloride are equivalent to 5·812 grms. of silver nitrate. Hence, when the standard silver nitrate solution contains 5·812 grms. of silver nitrate per litre, and 2 grms. of the sample are taken, every 10 c.c. of the silver nitrate solution will represent 1 per cent. of sodium chloride in the given sample.

§ 25. Hydrogen Ion Concentrations.

On the theory of electrolytic dissociation, the extremely low electrical conductivity of water is interpreted as evidence that water is dissociated only to a very slight extent. However, since even the purest water is not a perfect non-electrolyte, some dissociation must have occurred and different experimental methods indicate that a litre of the purest water obtainable contains at 25° C. approximately 1×10^{-7} gram-ion of hydrogen.

If the law of mass action be applied, it follows that $C_H \times C_{OH} = KC_{H_2O}$ but, as water is so slightly ionised, C_{H_2O} can be taken as constant, hence $C_H \times C_{OH} = K_W$ where K_W is the ionic product for water. Now as the water must contain an equal number of hydrogen and hydroxide ions, $C_H = C_{OH}$, whence $K_W = 1 \times 10^{-14}$ at 25° C.

For arithmetical convenience and for no other reason, the logarithm of the reciprocal of the actual concentration of the hydrogen ion present in a solution is taken as a measure of the concentration of that ion. The numbers so obtained are termed the hydrogen ion concentrations and are denoted by the symbol p_H. Thus, for pure water, as there is 1×10^{-7} gram-ion of hydrogen per litre, the hydrogen ion concentration will be log $(1/10^{-7}) = 7.0$.

Assume now that a solution contains $(1 + n) \times 10^{-7}$ gram-ion of hydrogen per litre, where n is a positive number less than unity. Then the concentration of hydroxide ions will be $(1/1 + n) \times 10^{-7}$, since the product of the two must be equal to 1×10^{-14}. As n is positive $(1 + n)$ is greater than, and $(1/1 + n)$ is less than, unity, $i.e.$ the solution contains an excess of hydrogen ions, or in other words it is acidic. The hydrogen ion concentration of the solution will be given by $p_H = \log [1/(1 + n) \times 10^{-7}] = \log 10^7 - \log (1 + n) = 7 - \log (1 + n)$. But as $(1 + n)$ is a positive number greater than 1, $7 - \log (1 + n)$ will be less than 7. Consequently, for any solution in which hydrogen ions predominate, the value of p_H will be less than 7 and the greater the extent to which these ions predominate ($i.e.$ the greater the acidity of the solution), the smaller will be the p_H value of the solution until in the limit it approaches zero.

Conversely, if n is negative, $(1 + n)$ will be less than, and $1/(1 + n)$ greater than, unity, so that the concentration of hydrogen ions, $(1 + n) \times 10^{-7}$, will be less than that of the hydroxide ions, $(1/1 + n) \times 10^{-7}$, and the solution will be alkaline. In this case the p_H value of the solution will be given by log $[1/(1 + n) \times 10^{-7}]$, or $7 + \log 1/(1 + n)$, but as $1/(1 + n)$ is greater than 1, log $1/(1 + n)$ will be positive and $7 + \log 1/(1 + n)$ will be greater than 7. Thus, all alkaline solutions will have p_H values greater than 7 and, as the alkalinity of the solution progressively increases, the p_H value rises to the limiting value of 14.

In summary, the acidity or alkalinity of a solution can be expressed quantitatively by a scale of numbers ranging from 0 to 14. All truly neutral solutions have a value (p_H value) of 7 on this scale; the values for acid solutions lie between 7 and 0, and for alkaline solutions between 7 and 14. The higher the acidity of a solution the lower is its number on the scale, and the greater the alkalinity of a solution the higher is its scale number.

§ 26. The Theory of Acid-Alkali Titrations. Indicators.
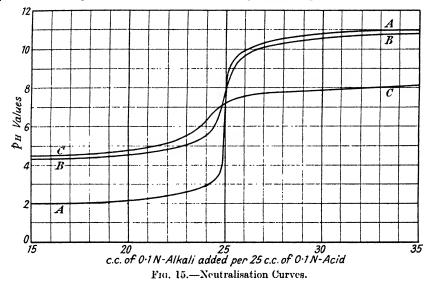
The stoichiometric or equivalence point is that point at which an equivalent of the reacting substance has been added, as calculated from the equation expressing the course of the reaction, irrespective of the type of reaction involved. The end-point in an acid-alkali titration is that point at which the titration is stopped, being shown by the colour change of the particular indicator used.

The suitability or otherwise of an indicator in any given titration depends upon the p_H value at which the indicator shows its specific colour change.[1]

Let, say, 15 c.c. of a 0·1N-solution of a base be added to 25 c.c. of a 0·1N-solution of an acid and the solution be made up to some standard volume so dilute that the electrolytes present are totally or almost completely dissociated. If, now, a series of similar solutions be made up, each of which contains a slightly greater amount of base than the one preceding it, and the p_H value of each solution be determined, then data will be obtained from which a graph can be drawn between the p_H value of the solution and the volume of alkali added.

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[1] For the theory of the titration error, see S. Kilpi, *Zeit. anal. Chem.*, **104**, 390, 1936; H. Arnfelt, *Svensk Kem. Tid.*, **49**, 96, 1937.

When a strong monobasic acid is progressively neutralised by a strong monacid base, the type of curve obtained is shown by Graph A in fig. 15. If, however, the acid is a weak one, the graph is of the form B; while Graph C illustrates the neutralisation curve when both the acid and the base are weak. It will be seen that the essential difference between the three curves is the rate at which the p_H value of the solution changes with respect to small additions of base in the neighbourhood of the equivalence point. Where this change is rapid, the section of the curve through the equivalence point becomes approximately parallel to the p_H axis. In such cases the equivalence point can be accurately

FIG. 15.—Neutralisation Curves.

determined if we can tell when the p_H value of the solution falls within that section of the curve which is parallel to the p_H axis.

These conditions are fulfilled when a strong monobasic acid is neutralised by a strong monacid base. Thus, in Graph A any indicator which shows its specific colour change within the range p_H 4 to 9 will give an end-point in close agreement with the equivalence point, provided the volume of alkali used is large in comparison with the difference between the volume of alkali corresponding to the equivalence point and the volume actually added.[1] When a weak acid is neutralised by a strong base (Graph B) a similar approximation of the end-point to the equivalence point will be obtained only when an indicator is used the colour of which changes within a range of about p_H 7 to 8·5. Finally, when both acid and base are weak, the change in p_H value round the equivalence point is so gradual that only an indicator changing colour within the very limited range of p_H 7·2 to 7·4 would give reasonable coincidence between the end and the equivalence points. Under such conditions the equivalence point cannot in general be located accurately by the use of an indicator.

The annexed table gives a list of some commonly used indicators and their colour changes on passage from acid to alkaline solution. In the third column is given the least p_H range over which the colour change can be detected visually under daylight illumination when 2 to 4 drops of indicator are used per 100 c.c.

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[1] Otherwise this difference, the titration error, will be comparable in magnitude with the total volume of alkali added.

Table X.—Indicator Colour Changes.

Indicator.	Colour change, acid - > alkaline.	Minimum p_H range.	Extreme p_H range.
Methyl violet [1]	Yellow → violet	0·4 to 1·0	0·1 to 3·2
Bromophenol blue	Yellow → violet	3·2 ,, 4·0	2·8 ., 4·6
Methyl orange	Pink - > yellow	4·4 ., 4·6	2·9 ., 4·6
Methyl red	Pink > yellow	4·8 ., 5·4	4·2 ., 6·3
p-Nitrophenol	Colourless - > yellow-green	5·0 ., 5·8	5·0 ,, 7·0
Litmus [2]	Red > blue	5·0 ,, 6·0	5·0 ., 8·0
Bromocresol purple	Grey -> purple	5·8 ,, 6·2	5·2 ., 6·8
Bromothymol blue [3]	Yellow-green - - blue	6·4 ., 7·0	6·0 ., 7·6
Phenol red	Yellow > red	7·0 ., 7·4	6·8 ., 8·4
Cresol red	Yellow > lilac	7·6 ., 8·2	7·2 ., 8·8
Phenolphthalein	Colourless > red	7·8 ., 8·0	7·8 ., 10·0
Thymolphthalein	Colourless > blue	7·9 ., 8·9	7·9 ., 10·5
Thymol blue [4]	Grey green - blue	8·4 ., 9·2	8·0 ., 9·6

of solution. The extreme p_H range is that range within which each particular indicator can be usefully employed.[5]

Reference to the table shows that methyl orange is pink at p_H 4·4 and yellow at p_H 4·6 while phenolphthalein is colourless at p_H 7·8 and red at p_H 8·0. Hence in titrating a strong monobasic acid with a strong base either methyl orange or phenolphthalein can be used, since the colour changes of both indicators fall within the range p_H 4 to 9 (Graph A, fig. 15). With methyl orange the end-point will be shown slightly before the equivalence point is reached and with phenolphthalein slightly after.[6]

When a weak acid is under titration (Graph B), phenolphthalein, but not methyl orange, will give an end-point in close agreement with the equivalence point.

A large variety of indicators is available for volumetric analysis, but here only a limited number will be discussed.[7] The light is an important matter in

[1] Green colour given at p_H 0·6.   [2] Litmus is purple at p_H 5·5.
[3] Green colour given at p_H 7·0.
[4] Pink at p_H 2·0, salmon at p_H 2·4, and yellow at p_H 2·8.
[5] For the constitution of various indicators, their correct concentrations for use and their p_H range, see H. A. Fales, *Inorganic Quantitative Analysis*, London, 143, 1928; I. M. Kolthoff, *Pharm. Weekb.*, **66**, 67, 1929; H. W. van Urk, *ib.*, **65**, 1246, 1928.
[6] The inference is that if duplicate titrations be made with each indicator in turn, the mean of the readings for the two end-points will very closely approximate to the equivalence point. Phenol red, with a least p_H range of 7·0 to 7·4, will give a more accurate value than either methyl orange or phenolphthalein.
[7] F. Glaser, *Indikatoren der Acidimetrie und Alkalimetrie*, Wiesbaden, 1901, and A. I. Cohn, *Indicators and Test-papers*, New York, 1899, deal with those proposed up to time of publication. For the theory of indicators, see the text-books on physical chemistry, or J. W. Mellor, *Chemical Statics and Dynamics*, London, 216, 1909; E. Salm, *Zeit. Elektrochem.*, **10**, 341, 1904; **12**, 99, 1906; *Zeit. phys. Chem.*, **57**, 471, 1906; R. Wegscheider, *ib.*, **90**, 641, 1915; G. F. Hüttig, *ib.*, **95**, 280, 1920; F. Liebert, *Chem. Weekb.*, **12**, 1088, 1915; A. A. Noyes, *Journ. Amer. Chem. Soc.*, **32**, 815, 1910; H. A. Lubs and S. F. Acree, *ib.*, **38**, 2772, 1916; A. B. Clark and H. A. Lubs, *ib.*, **40**, 1443, 1918; A. Thiel, *Chem. Zentr.*, (1), 653, 1913; (1), 423, 1914; J. Waddell, *Chem. News*, **107**, 206, 1913; A. G. A. Miller, *ib.*, **108**, 73, 1913; A. Hantzsch, *Ber.*, **48**, 158, 1915; A. Grünberg, *Zeit. anorg. Chem.*, **138**, 333, 1924; H. A. Lubs and W. M. Clark, *Journ. Wash. Acad. Sci.*, **5**, 609, 1915; **6**, 481, 1916; S. P. L. Sörensen and S. Palitzsch, *Biochem. Zeit.*, **24**, 381, 1910; F. M. Cray and G. M. Westrip, *Trans. Faraday Soc.*, **21**, 326, 1925; C. J. van Nienwenburg, *Chem. Weekb.*, **27**, 143, 158, 186, 206, 1930; R. T. Thomson, *Chem. News*, **47**, 123, 184, 1883; **49**, 32, 119, 1884; **52**, 18, 29, 1885; A. H. Allen, *Analyst*, **17**, 186, 215, 1892; **39**, 518, 1914; I. M. Kolthoff, *Ind. Eng. Chem. Anal.*

volumetric work. A window facing the north is best. The colour changes of indicators often appear different when examined in gaslight. To one accustomed to work in daylight, the "transition tints" of some indicators may be misleading when viewed in yellowish artificial light. Incandescent and electric light are not very different from daylight. Direct sunlight is objectionable. It is generally best to use an Erlenmeyer's flask over a white tile or sheet of white paper. It is often an advantage to work with two vessels the same size as the vessel in which the titration is to be made. Each contains about the same volume of liquid and the same amount of indicator as the vessel containing the solution under investigation. In one, the colour change has been effected. The two vessels, one containing the changed and the other the unchanged indicator, are useful for comparison until the eye has become accustomed to the tints of the indicator. It is sometimes advisable, in cases of uncertainty, to read the burette; if the addition of another drop of the standard solution alters the intensity but not the tint of the indicator, it is not included in the titration. In some cases the titration is continued until the change of tint is quite certain, and then the solution is titrated back with the proper standard solution to determine the exact end-point.

1. *Litmus.* · Litmus is sold in the form of cakes, cubes or granules. It is one of the oldest indicators, and even now it is still frequently used. An aqueous solution of litmus is blue in the presence of a slight excess of alkalies or alkaline earths; the solution is coloured red in the presence of a slight excess of acid. The neutral solution is violet. The instability of its aqueous solution is the main objection to litmus. The solution does not keep very well.[1] The sensitiveness of the solution prepared by digesting commercial litmus in water is not the best possible, since the litmus contains at least two distinct colouring principles - one a very sensitive violet colour and the other a red colour of feeble sensitiveness. The latter obscures the tints of the violet principle. Püschel[2] isolates the violet colouring principle as follows:—

Digest 100 grms. of commercial litmus with 600 c.c. of hot distilled water, and after allowing the mixture to stand for some time, decant the solution from the sediment.[3] After standing for a few more days, the solution is again decanted from any sediment. Evaporate the solution in a porcelain basin down to about 200 or 250 c.c. Filter the solution while hot into a half-litre flask. Make the filtrate up to about 300 c.c. with distilled water. Mix 50 c.c.

Ed., 8, 237, 1936; E. Salm and H. Friedenthal, *Zeit. Elektrochem.*, 13, 125, 1907; N. Bjerrum, *Die Theorie der alkalimetrischen und azidimetrischen Titrierungen*, Stuttgart, 1914; *Zeit. anal. Chem.*, 56, 13, 81, 1917; H. Brückner, *ib.*, 99, 427, 1934; T. Kaku, *Journ. Pharm. Soc. Japan*, No. 518, 63, 1925; W. M. Clark, *The Determination of Hydrogen Ions*, Baltimore, 1928; H. Eichler, *Monats.*, 70, 79, 1937; M. Deribéré, *Industrie chimique*, 24, 305, 1937; A. E. Jennings, junr., *Can. Chem. Met.*, 20, 220, 1936; J. V. Dubský and A. Langer, *Chem. Obzor.*, 11, 29, 1936.

[1] The commercial article contains a gelatinous substance which acts as a good medium for the growth of fungi and bacteria. R. Dubois, *Bull. Soc. Chim.*, (2), 49, 763, 1888; A. Vogel, *Journ. Pharm. Chim.*, 45, 70, 1864; *Chem. News*, 9, 205, 1864; B. Balli, *Chem. Ztg.*, 15, 68, 1191, 1896. If sterilised, the solution does not change so readily. Phenol, thymol and chloroform have been recommended for this purpose.

[2] A. Püschel, *Oester. Chem. Ztg.*, 13, 185, 1910; M. Kretzschimar, *Chem. Ztg.*, 3, 682, 1879; K. Mays, *Chem. Centr.*, (3), 17, 99, 1886; V. de Luynes, *Chem. News*, 11, 149, 1865; V. Wartha, *Ber.*, 9, 217, 1876; B. Reinitzer, *Zeit. angew. Chem.*, 7, 547, 1894; O. Förster, *Zeit. anal. Chem.*, 28, 428, 1889; P. Scheitz, *ib.*, 49, 735, 736, 1910; W. Schäfer, *Apoth. Ztg.*, 9, 839, 1894; E. W. Rice, *Journ. Ind. Eng. Chem.*, 4, 229, 1912.

[3] The solution will take no harm if the temperature be kept below about 6°. The bacteria grow only at higher temperatures than this. Hence, this work is best done during the winter months.

of distilled water with 16 grms. of pure concentrated sulphuric acid in a separate flask and make the solution up to about 100 c.c. Mix the two solutions, and digest the mixture on a water bath, with frequent agitation, for about 4 hours. A dark brownish-red gelatinous precipitate gradually separates.[1] When cold, filter through a 12·5 cm. filter-paper. Wash the precipitate with cold distilled water until the washings give no reaction for sulphate with barium chloride. The precipitate still contains some of the red colouring principle and the gelatinous matter. The washing is therefore continued in order to remove the former. The wash-water has a faint red colour which gives a violet colour with potash solution as long as the red colouring principle remains. When the wash-water gives a dark blue colour with potash,[2] it is supposed that nearly all the red colouring matter is washed away. The precipitate is then digested in dilute alcohol by pouring 100 c.c. of warm 90 per cent. alcohol, in small quantities at a time, through the filter-paper. The colouring principle passes into solution, the gelatinous matter remains behind. Collect the washings in a porcelain basin. Add a drop of ammonia to the later portions of alcohol which are passed through the paper. Finish the washing with pure alcohol. Evaporate the solution to dryness on a water bath. Dissolve the residue in hot distilled water. Filter. Make the solution up to 600 c.c. Divide the red solution into two approximately equal portions. Neutralise the one portion with a dilute solution of caustic potash. The solution then becomes blue. Mix the two solutions. Again divide the solution into two portions, and repeat the operation until the solution has a neutral violet tint.[3] This solution does not change on keeping in glass-stoppered bottles.[4]

Litmus solution is quite satisfactory for the titration of caustic alkalies, alkaline earths and ammonia; also for hydrochloric, sulphuric, nitric and oxalic acids. It can only be used with carbonates or bicarbonates when the liberated carbon dioxide is driven off by boiling the solution. The dissolved gas in cold solutions causes the red colour to persist even when the titration is completed. Hence, although quite satisfactory in *boiling* solutions of the carbonates, litmus should not be used with *cold* solutions. Similar remarks apply to the sulphides. Litmus can also be used for titrating arsenites and silicates, but not for titrating sulphurous, phosphoric, arsenic, boric and chromic acids. It is also useless for titrating most organic acids, *e.g.* tartaric and citric acids.

2. *Phenolphthalein.*—The solution of phenolphthalein is made by dissolving 0·5 grm. of phenolphthalein in 500 c.c. of absolute alcohol and making the solution up to a litre with water. Use 2 to 4 drops per 100 c.c.

Phenolphthalein solution is nearly colourless in neutral and acid solutions, but red in the presence of a slight excess of alkali. It is used in titrating the hydroxides of the alkalies and alkaline earths, the mineral acids and most organic acids. It does not work satisfactorily in the presence of ammonia, ammonium salts and alcohol; nor does it give satisfactory results with arsenious, silicic and boric acids. It is very sensitive to carbonic acid and

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[1] Presumably a sulpho-salt of the violet colouring matter.

[2] A sensitive eye can tell when the washing is finished by the fiery red tint of the washings.

[3] A neutral solution appears violet by transmitted light. It is coloured red by a trace of acid and blue by a trace of alkali.

[4] Litmus paper is made by coating one side of a sheet of pure white paper with a solution of one part isinglass in 50 c.c. of water. When dry, coat the isinglass with the litmus solution —A. Vacher, *Chem. News*, 17, 277, 1868; F. Mohr, *Zeit. anal. Chem.*, 12, 368, 372, 1893. The "*dupli-test litmus papers,*" with a strip of blue and of red litmus separated by a thin strip of ceresine or paraffin, are very convenient for finding if a solution is "acid" or "alkaline"— K. Dietrich, *Zeit. angew. Chem.*, 14, 1091, 1904.

hydrogen sulphide, but it appears neutral when the acid salts have been formed. Hence, phenolphthalein may be used to detect sodium carbonate in the presence of sodium bicarbonate. It also appears neutral with arsenic and phosphoric acids when two-thirds of the hydrogen has been replaced.[1]

3. *Methyl Orange.*— The solution is prepared by dissolving 1 grm. of methyl orange in a litre of water.

The indicator is orange-yellow in neutral or alkaline solutions, and it changes to pink with a slight excess of acid. The end-point with methyl orange is not so sharp as with phenolphthalein, since methyl orange shows several shades of colour—"transition tints." This trouble, however, is aggravated by the use of too much indicator. Two drops of the above solution are sufficient to give a distinct yellow to a solution.[2] If the colour fades during a titration, add another drop of the indicator.

Methyl orange is not so suitable for titrations in the presence of methyl alcohol as *p*-nitrophenol. Methyl orange is almost, but not quite, indifferent to

Fig. 16.—Nest of Pipette Bottles for Indicators.

the presence of carbonic acid, but less so than nitrophenol. The amount of carbonic acid which remains in solution during the titration of, say, 0·2N-carbonate solutions exerts an appreciable effect on the colour of methyl orange. Küster recommends adjusting the colour of the solution obtained on titration to that of a saturated aqueous solution of carbonic acid containing methyl orange.[3] It is also practically indifferent towards aqueous solutions of hydrogen sulphide, arsenious, boric, silicic and hydrocyanic acids. It can be used for the strong mineral acids, hydroxides of the alkalies and alkaline earths, ammonia, carbonates, sulphides, arsenites, silicates and borates which are decomposed by dilute nitric, hydrochloric or sulphuric acid. Phosphoric and

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[1] H. N. and C. Draper, *Chem. News*, 55, 133, 143, 1887; J. H. Long, *ib.*, 51, 160, 1885; P. Dobrenier, *Zeit. angew. Chem.*, 8, 259, 1895; F. Scheiding, *ib.*, 8, 78, 1895.

[2] R. T. Thomson (*Chem. News*, 47, 123, 1883) recommends a solution containing 0·15 grm. per litre, and uses 0·5 c.c. of this solution per 100 c.c. of the solution to be titrated.

[3] F. W. Küster, *Zeit. anorg. Chem.*, 13, 141, 1897. G. P. Baxter (*Journ. Amer. Chem. Soc.*, 36, 656, 1914) recommends a solution of monosodium phosphate ($NaH_2PO_4.2H_2O$, crystallised between 0° and 41°—A. Imadsu, *Mem. Coll. Science Eng., Kyoto*, 3, 257, 1912) containing 15 grms. of the crystals per 100 c.c. of water in place of the saturated solution of carbonic acid; 15·3 grms. of crystals of the monopotassium phosphate, KH_2PO_4, can also be used instead of 15 grms. of the sodium salt.

arsenic acids become neutral to this indicator when one-third of their replaceable hydrogen has reacted with the alkali and sulphurous acid becomes neutral when the acid sulphite is formed. Methyl orange is not to be used for the organic acids. Solutions containing nitrous acid or nitrites destroy the colour. It must be used in cold, not hot, solutions, since the end-point becomes indistinct and loses its sharpness when titrations are made in hot solutions. If it be desired to eliminate the slight effect of carbon dioxide on methyl orange in titrating the carbonates, the solutions may be boiled when nearly neutralised, and the titration finished when the solution is cold.

Indicators are conveniently kept in bottles fitted with a pipette, in order that the indicator may be removed without contact with the stain which usually collects about the necks of the bottles when the solutions are transferred in the ordinary manner. This stain interferes with the sharpness of the end-point—*e.g.* methyl orange in the bromate process for antimony. A nest of four pipette bottles for the most commonly used indicators is illustrated in fig. 16. The indicators, when kept in this way, are easily carried from bench to bench.

§ 27. Standard Solutions of Sodium Hydroxide.

Sodium hydroxide—NaOH. Molecular weight: 40·005;
equivalent weight: 40·005.

The most commonly employed solutions are:—

					Grm. NaOH per c.c.
N-Sodium hydroxide	.	.	.	.	0·040005
0·5N-Sodium hydroxide	.	.	.	.	0·0200025
0·2N-Sodium hydroxide	.	.	.	.	0·008001
0·1N-Sodium hydroxide	.	.	.	.	0·0040005

Sodium hydroxide does not make an ideal standard solution, since it is liable to absorb carbon dioxide from the air.[1] A solution of sodium hydroxide is also particularly liable to attack glass, and gradually to lose its strength. In consequence, it is not usually advisable to make up a large stock of the solution. Küster recommends storing sodium hydroxide in nickel bottles. Glass stoppers and glass stopcocks are also objectionable because they are liable to seize up. It is therefore advisable to use rubber stoppers and rubber plug cocks with the burettes working caustic lyes.

To prepare a half-normal solution of sodium hydroxide, select a number of clear sticks of sodium hydroxide, " pure by alcohol." Scrape off the opaque parts; dissolve, say, 25 grms. in water and make the solution up to 1100 c.c. in a Giles' flask. Recently boiled distilled water must be used in order to keep out the carbon dioxide. When the solution has cooled to 15°, pipette 25 c.c. into an Erlenmeyer's flask;[2] add two or three drops of methyl orange

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[1] T. Milobedski and W. Szczypinski, *Roczniki Chem.*, **14**, 1088, 1934. E. Fleischer (*Chem. News*, **19**, 203, 1869), in consequence, prefers a 0·5N-ammonia solution as a standard alkali. If solutions over this strength be used, they are liable to change, owing to the loss of ammonia; and even 0·5N-solutions are liable to lose ammonia on a hot summer's day, when the temperature is, say, 25°. There is also a difficulty with some of the indicators when ammonia solutions are used. R. Rempel, *Chem. Ztg.*, **9**, 1906, 1884; E. Altmann, *ib.*, **37**, 1465, 1913; G. T. Gerlach, *Chem. Ind.*, **12**, 97, 1889; W. G. Haynes, *Ind. Eng. Chem.*, **9**, 58, 1917.

[2] The liquid should be thoroughly agitated during the titration. An Erlenmeyer flask is generally preferable to ordinary narrow-necked flasks, to beaker and glass rod, or to basin and glass rod, because its contents are so accessible and so easily agitated without stirring.

solution as indicator; run 0·5 N-acid from the burette until the yellow colour of the methyl orange changes to an orange colour. Read the burette. Continue the titration, drop by drop, until the addition of a single drop of acid turns the solution pink.[1] Again read the burette. Repeat the titration with two more portions of 25 c.c. Let 26·42 c.c. denote the mean volume of the acid used in the titration, then 25 c.c. of the sodium hydroxide solution contains an amount of alkali corresponding with 26·42 c.c. of 0·5N-acid. If the alkali had been exactly 0·5N, like the acid, 25 c.c. of acid would have been used.

Thus, every 25 c.c. of the alkali needs the addition of $26·42 - 25 = 1·42$ c.c. of water to dilute it to 0·5N strength; consequently 1000 c.c. will need 56·8 c.c. of water. Hence, pipette alkali solution from the flask until the liquid stands at the 1000 c.c. mark, and add 56·8 c.c. of water in order that the alkali may be exactly half-normal. Verify the accuracy of the dilution by repeating the titration.

Fig. 17.—Burette with Guard Tube.

Excellent results are obtained by using the modified methyl orange indicator recommended by Hickman and Linstead.[2] Dissolve 1 grm. of methyl orange and 1·4 grms. of xylene cyanole FF in 500 c.c. of 50 per cent. alcohol: use two or three drops for a titration. In alkaline solution the colour is green and in acid solution magenta, while at the neutral point it is grey without any trace of green or magenta.

In the case of boric oxide titrations special care must be taken to exclude carbon dioxide. The burette and stock solution should be well protected from atmospheric carbon dioxide by using a soda-lime [3] tube as indicated in fig. 17. To test if the solution is really free from carbonates, make two parallel titrations with phenolphthalein as indicator. If the one solution be hot and the other cold, carbonates will be absent if the two results agree. If otherwise, carbonates are present.

Guard Tubes.—Standard solutions liable to absorb oxygen, *e.g.* stannous chloride and titanous chloride, can be kept in an atmosphere of hydrogen by connecting the air tube with a small apparatus for generating hydrogen whenever the pressure in the bottle is reduced below atmospheric.[4] This can easily be done by means of a perforated boiling-tube containing metallic zinc and an acid jar, as shown in fig 70, page 183. These are fitted together like many of

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[1] At first, it is best to work with comparison flasks, as described on page 49.

[2] K. C. D. Hickman and R. P. Linstead, *Journ. Chem. Soc.*, **121**, 2502, 1922. Compare F. X. Moerk, *Amer. Journ. Pharm.*, **93**, 675, 1921; G. Chabot, *Bull. Soc. chim. Belg.*, **34**, 202, 1925; S. Hähnel, *Svensk Kem. Tids.*, **47**, 4, 1935; M. S. Kovtun, *Zavodskaya Lab.*, **6**, 229, 1937.

[3] E. Fleischer (*Chem. News*, **19**, 303, 1869) prefers a mixture of Glauber's salt and caustic lime. A. Beutell, *Chem. Ztg.*, **12**, 86, 1887.

[4] A. Sauer, *Zeit. anal. Chem.*, **12**, 177, 1873; R. Fresenius, *Quantitative Chemical Analysis*, London, **1**, 226, 1876; R. H. Ridout, *Chem. News*, **29**, 3, 1874; G. S. Johnson, *ib.*, **57**, 213, 1888; H. C. Coram, *ib..* **57**, 241, 1888; E. Douzard, *ib.*, **83**, 18, 47, 1901; Sorge, *Chem. Ztg.*, **5**, 145, 1880; E. Knecht and E. Hibbert, *New Reduction Methods in Volumetric Analysis*, London, **47**, 1918; F. Resch, *Zeit. Oester. Apoth. Ver.*, **44**, 159, 1906; C. J. van Ledden Hulsebosch, *Pharm. Weekb.*, **43**, 1309, 1906; A. Scholl, *Zeit. Nahr. Genuss.*, **15**, 343, 1908; M. E. Pozzi-Escot, *Bull. Assoc. Chim. Sucr. Dist.*, **25**, 1077, 1908; M. von Heygendorff, *Pharm. Ztg.*, **54**, 159, 1909; S. Chumanoff, *Journ. Russ. Phys. Chem. Soc.*, **44**, 566, 1912; H. Mannhardt, *Journ. Amer. Chem. Soc.*, **27**, 299, 1905; C. J. Schollenberger, *Ind. Eng. Chem. Anal. Ed.*, **7**, 199, 1935.

the small hydrogen sulphide generators—*e.g.* Coram's or Johnson's.   Mohr [1] recommended covering the solution with a layer of petroleum in order to prevent evaporation, oxidation, or the absorption of carbon dioxide by standard solutions of caustic alkalies, barium hydroxide, sulphites, etc.   Morgan,[2] however, has shown that refined petroleum permits a comparatively rapid diffusion of oxygen from the air to the solution. The oxygen acts deleteriously on solutions of stannous chloride.   He considers Sorge's suggestion to keep the bottle permanently connected with the coal-gas supply is better than keeping a layer of petroleum over the surface of the solution.

Fig. 18.—Blochmann's Guard Tubes.
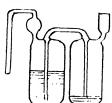
Fig. 19.—Göckel's Guard Tubes.

With solutions of caustic alkalies and barium hydroxide, which rapidly absorb carbon dioxide from the air, the air tube should be connected with a U-tube containing soda-lime, so that all communication with the air must be made *via* this absorption tube.   Blochmann's [3] arrangement (fig. 18) for this purpose is excellent.   The air tube is connected with a test tube containing 5 to 10 c.c. of dilute (approximately 0·02N) caustic potash coloured with a drop of phenolphthalein.   The test tube is also connected with a soda-lime tube, as shown in the diagram.   The test tube with the potash serves to indicate the efficiency of the soda-lime.   Göckel's tube is rather neater (fig. 19).   This may be attached both to the burette and to the stock solution, and charged with any desired solution.

Preparation of Sodium Hydroxide Solutions Free from Sodium Carbonate.— The following process is recommended by Cornog.[4]   Boil distilled water in

[1] F. Mohr, *Zeit. anal. Chem.*, 8, 113, 1869.   C. Meineke and K. Schröder (*Zeit. öffent. Chem.*, 3, 5, 1896) prefer vaseline oil.   With permanganate solutions, a small amount of manganese dioxide separates out at first, but after standing a couple of months, the vaseline oil is said to have no appreciable effect on the strength of the solution. H. Mannhardt (*Journ. Amer. Chem. Soc.*, 27, 299, 1905) recommends two wash-bottles, one with yellow phosphorus and the other with water, for cutting off oxygen from oxidisable solutions, *e.g.* SnCl₂.

[2] F. H. Morgan, *Journ. Anal. App. Chem.*, 2, 164, 1888; B. Pawolleck, *Ber.*, 16, 3008, 1883.   S. Gneiwosz and A. Walfisez (*Zeit. phys. Chem.*, 1, 70, 1887) have shown that the absorption coefficient of petroleum for oxygen is greater than that of water.

[3] R. Blochmann, *Liebig's Ann.*, 237, 39, 1887; H. Göckel, *Chem. Ztg.*, 35, 279, 1911; M. Lindt, *Met. Erz.*, 10, 139, 1912.

[4] J. Cornog, *Journ. Amer. Chem. Soc.*, 43, 2573, 1921.   For other methods, see F. W. Küster, *Zeit. anorg. Chem.*, 13, 134, 1897; 41, 474, 1904; W. A. Smith, *Zeit. phys. Chem.*, 25, 155, 1898; H. Ley, *ib.*, 30, 205, 1899; W. R. Bousfield and T. M. Lowry, *Phil. Trans.*, 204, 253, 1905; E. Neitzel, *Zeit. anal. Chem.*, 32, 422, 1893; W. Stahl, *ib.*, 97, 86, 1934; F. Pregl, *ib.*, 67, 25, 1925–26; I. M. Kolthoff, *ib.*, 61, 48, 1922; *Pharm. Weekb.*, 58, 1413, 1921; S. P. L. Sörensen, *Biochem. Zeit.*, 21, 186, 1909; W. P. Jorissen and H. Filippo, junr., *Chem. Weekb.*, 6, 145, 1909; *Zeit. angew. Chem.*, 23, 726, 1910; W. N. Hartley, *Journ. Chem. Soc.*, 26, 123, 1873; C. P. Hopkins, *Journ. Amer. Chem. Soc.*, 23, 727, 1901; A. Findlay, *Practical Physical Chemistry*, London, 173, 1928; W. W. Kay and H. L. Sheehan, *Biochem. Journ.*, 28, 1795, 1934; N. Allen and G. W. Low, junr., *Ind. Eng. Chem. Anal. Ed.*, 5, 192, 1933; J. E. S. Han and T. Y. Chao, *ib.*, 3, 379, 1931; 4, 229, 1932.   For explosions during the preparation of standard sodium hydroxide from metallic sodium, see A. Harpf and H. Fleissner, *Zeit. chem. Apparatenkunde*, 1, 534, 1906; F. W. Küster, *ib.*, 2, 535, 1906.   For the preparation of colourless alcoholic solutions of potassium hydroxide, H. Thiele and R. Marc (*Zeit. öffent. Chem.*, 10, 386, 1904) recommend the use of potassium sulphate and barium hydroxide.   See R. Gaze, *Apoth. Ztg.*, 25, 668, 1910.

an Erlenmeyer flask until it is free from carbon dioxide. Close the flask with a soda-lime guard-tube and cool to room temperature. Then add ether until it forms a layer 3–4 cm. deep on the surface of the water. Next weigh out about the requisite quantity of unoxidised metallic sodium, freed from naphtha by pressing between folds of filter-paper. Add the sodium gradually to the ether, in pieces *not exceeding* 1 cm. in diameter. When all the sodium has been added, remove the bulk of the ether by a pipette and finally boil off the remainder. The layer of ether must be sufficiently deep to prevent the sodium coming into simultaneous contact with air and water, otherwise the reaction will become violent. If the ether evaporates appreciably owing to the heat of the reaction, add more from time to time.

If the temperature of the soda solution be more than 3° different from the standard temperature an allowance must be made for expansion or contraction. The following correction table [1] (Table XI.) is used, as has been indicated by example, Tables VI. and IX. (pages 22 and 40). For solutions more dilute, say 0·1N, the table for water (page 22) is used.

Table XI. Temperature Corrections for Normal Soda Solutions.
(Standard temperature, 15°.)

Temp.	0	1	2	3	4	5	6	7	8	9
	..	..	..	..	..	+2·0	+1·9	+1·7	+1·5	+1·3
10	+1·1	+0·9	+0·7	+0·5	+0·3	Zero.	−0·2	−0·5	−0·7	−1·0
20	−1·3	−1·5	−1·8	−2·1	2·4	·2·7	−3·0	−3·4	−3·7	−4·0

§ 28. The Errors of Experiment in Volumetric Analysis.

The principal errors incidental to volumetric work [2] are: (1) unrecognised changes in the strength of the standard solutions; (2) inaccurate measuring instruments (page 29)—with care, these can usually be kept below 0·1 per cent.; (3) in weighing the substances used in the analysis (page 19)—the errors in weighing need not exceed 0·1 per cent.; (4) the use of dirty burettes, and drainage errors previously discussed; and (5) a small excess of the standard solution is needed before the indicator will show the end of the reaction—this error is somewhat variable in magnitude and depends upon a number of factors. For instance, it depends upon the amount and concentration of the standard solution used in the titration and on the magnitude of the drops falling from the burette. In the regular types of burette, one drop is nearly 0·05 c.c. Hence, if the reaction be not completed on the addition of the last drop, and completed with the addition of one drop more, it is often assumed that half a drop, namely, 0·025 c.c., completed the reaction. [3]

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[1] This table may also be used for $N-H_2SO_4$; $N-HNO_3$; $N-Na_2CO_3$; $N-NaOH$. It is based on A. Schulze, *Zeit. anal. Chem.*, **21**, 167, 1882, and it can be easily adapted to other standard temperatures.

[2] For the theory of the error of acid-alkali titrations, see H. N. McCoy, *Amer. Chem. Journ.*, **31**, 512, 1904; A. A. Noyes, *Journ. Amer. Chem. Soc.*, **32**, 815, 1910; P. S. Roller, *ib.*, **54**, 3485, 1932; H. T. Tizard and A. R. Boeree, *Journ. Chem. Soc.*, **119**, 132, 1921; H. A. Fales, *Inorganic Quantitative Analysis*, London, 127, 1928. See also section 26.

[3] In some processes, the "excess" of standard solution needed to produce a colour with the indicator is specially determined. This is done, for instance, in the uranium process for phosphorus (page 678), the ferrocyanide process for zinc (page 392,) and the chromate process for chlorides (page 69).

The smaller the amount of substance used in the analysis, the smaller the volume of the standard solution needed for the titration and the greater the error of experiment. If 4 c.c. of the standard solution be used, half a drop, namely, 0·025 c.c., may lead to an error of 0·62 per cent.; whereas, if 40 c.c. of the standard solution be needed for the titration, the corresponding error would be 0·062 per cent.

Again, suppose three independent determinations of the ferric oxide be made on 1 grm. samples of a given clay by titration with permanganate solution (1 c.c. representing 0·002527 grm. Fe_2O_3), and 1·0, 1·01 and 1·1 c.c. were respectively needed. The corresponding percentage amounts of ferric oxide would be respectively 0·2527, 0·2552 and 0·2780 grm. Suppose, further, that with another sample of clay 10·0, 10·01 and 10·1 c.c. of permanganate were needed in three independent titrations. The corresponding percentage amounts of ferric oxide would be 2·527, 2·529 and 2·552 grms. respectively. Again, suppose that 100·0, 100·01 and 100·1 c.c. of permanganate were needed with a third sample of clay. The corresponding amounts of ferric oxide would be 25·270, 25·272 and 25·295 grms. Hence, the greater the volume of the standard solution used in the titration, the less the effect of small deviations in the measurement of the volume of the standard solution on the final result.

Consequently, *it is advisable to arrange the quantity of substance to be analysed, and the strength of the standard solution, so that a comparatively large volume of the standard solution is used.* Since 50 c.c. burettes are generally used, something rather less than 50 c.c. is a convenient amount. For instance, 5 c.c. of concentrated hydrochloric acid (sp. gr. 1·14) will require about 44 c.c. of N-NaOH solution.[1] If an acid of sp. gr. 1·015 be in question, this has 32 grms. of HCl per 1000 c.c. Hence, 5 c.c. of this acid has 0·16 grm. of HCl. This would only take about 4·4 c.c. of N-NaOH. Hence, it is advisable to use a more dilute soda solution, say 0·1N-NaOH, in which case, about 44 c.c. of the standard solution will be needed. For the analysis of more dilute solutions of acid, more dilute solutions of alkali will be needed—say 0·01N-NaOH.[2] It does not follow that the weaker the standard solution the more accurate the titration, because, if the standard solution be too weak, a relatively large volume will be needed to colour the indicator after the end of the reaction, and nothing is really gained in accuracy.

The above principles can be discussed from another point of view. Suppose 2N-acid is used for the titration of a gram of sodium hydroxide, then 1 c.c. of the 2N-acid will represent 8 per cent. of NaOH, and 0·1 c.c. will represent 0·8 per cent. of NaOH. Unavoidable variations in the amounts of standard acid needed for the titration of duplicates will represent an error of 0·2 to 0·3 per cent. NaOH. This error is too great, and it is considerably reduced by using a standard acid but one-fourth the strength, namely, 0·5N-acid.

It is not advisable to make, say, 0·01N-NaOH by diluting 10 c.c. of 0·1N-NaOH to 100 c.c. unless the solution so obtained is standardised. This arises from the fact that a small error in the measurement of the volume of the concentrated solution is multiplied into a relatively large error by the process of dilution. For a similar reason, if a concentrated solution of hydrochloric

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[1] From gravity tables, 1000 c.c. of acid, sp. gr. 1·14, have 315 grms. HCl; consequently 5 c.c. will have 1·575 grms. HCl. Now since 36·5 grms. HCl react with 40·0 grms. NaOH, which are contained in 1000 c.c. of 1·0N-sodium hydroxide solution, 1·575 grms. HCl will react with 1·575 × 1000/36·5 = 43·1 c.c. of 1·0N-NaOH.

[2] To avoid refilling the burette frequently when many titrations have to be made, one of the various forms of automatic burettes can be used.

acid of, say, sp. gr. 1·14 is under investigation, and it is convenient to work with a dilute standard solution, say, 0·1N-NaOH, it is not advisable to take, say, 0·5 c.c. of the concentrated acid for the titration. Rather should 20 c.c. of the concentrated acid be made up to a litre, and 25 c.c. of this solution be used for the titration. The 25 c.c. of the diluted acid would represent 0·5 c.c. of the concentrated acid.

The reading is obviously the sharper, the narrower the burette. If the burette be narrow, it must have an inconvenient length if it is to hold enough liquid for a titration. A 50 c.c. burette reading to 0·1 c.c. will be about 60 cm. long, and the tube will have a bore of approximately 11 or 12 mm. In special cases, as in the colorimetric determination of iron, where a burette reading to 0·02 c.c. is used, the burette is about 0·5 cm. bore, with a capacity of 10 c.c., and yet is 75 cm. long.

These preliminary remarks may be used as a guide in the succeeding problems. For instance, to determine the amount of calcium carbonate in a sample of whiting, and the amount of calcium carbonate in a given sample of ground flint or ground Cornish stone. In the former case, the sample may have 98 per cent. of calcium carbonate and in the latter, 2 per cent. Since 50 grms. of calcium carbonate will correspond with 1000 c.c. of N-HCl, 1 grm. of calcium carbonate will correspond with 20 c.c. of N-HCl. Hence, if 50 c.c. of N-HCl be added to a gram of whiting, and the excess of HCl be titrated with N-NaOH, we shall need about 30 c.c. of the standard alkali. Again, 5 grms. of calcium carbonate will correspond with 1000 c.c. of 0·1N-HCl, and 1 grm. of calcium carbonate will correspond with 200 c.c. of 0·1N-HCl. Hence, if the ground flint contains 2 per cent. of calcium carbonate, 50 grms. of flint will want 200 c.c. of 0·1N-hydrochloric acid, or 5 grms. will want 20 c.c. of 0·1N-HCl. Hence, if 50 c.c. of 0·1N-HCl be mixed with 5 grms. of flint, the titration of the excess of acid will require about 30 c.c. of 0·1N-HCl.

§ 29. Direct Titrations—Sodium and Potassium Carbonates.

Suppose that it be required to determine the amount of sodium carbonate in a given sample of soda ash. A quantity of the powdered soda ash is placed in a weighing bottle and dried at 110°. When cold, the bottle and contents are weighed. A portion, approximately 1 grm., is transferred to an Erlenmeyer's flask, say 400 c.c. The weighing bottle and contents are again weighed. The difference between the two weights gives the amount of soda ash transferred to the flask:

Weighing bottle and powder (before)	.	.	.	25·2931 grms.
Weighing bottle and powder (after)	.	.	.	24·1110 grms.
Weight of soda ash	.	.	.	.	1·1821 grms.

Add about 150 c.c. of water. When all is dissolved, add about two drops of a solution of methyl orange and titrate the solution with 0·5N-HCl as indicated on page 52. Suppose that the experiment shows that 43·6 c.c. of the standard solution have been used. Then, since

$$Na_2CO_3 + 2HCl = 2NaCl + H_2O + CO_2$$

$2 \times 36·465$ grms. of hydrogen chloride react with 106·0 grms. of sodium carbonate. But since 1000 c.c. of the half-normal acid contain 36·465/2 grms. of hydrogen chloride, it follows that 4000 c.c. of this solution will react with 106·0 grms. of

sodium carbonate, or 1 c.c. of acid represents 0·0265 grm. of sodium carbonate. Thus 43·6 c.c. of the semi-normal acid represent $0·0265 \times 43·6 = 1·1554$ grms. of sodium carbonate per 1·1821 grms. of sample; hence the sample contains 97·74 per cent. of sodium carbonate.

All this arithmetic is summarised in the expression:

$$\frac{2·65n}{w} = \text{per cent. of Na}_2\text{CO}_3$$

where n represents the number of cubic centimetres of the 0·5N-HCl used in the titration, and w is the weight of sample used for the titration.

It will be obvious that if w be exactly 2·65 grms., the number of c.c. used in the titration will represent directly the percentage amount of Na_2CO_3 in the given sample.[1] It is sometimes most convenient to work according to the latter system (page 44). This question has to be solved: Is it quicker to weigh exactly the required amount, say, 1·325 grms., or to take an approximate weight and calculate the corresponding amount of sodium carbonate as indicated above? The answer will largely depend upon the number of determinations to be made and whether the weight of the substance is likely to change by the absorption of moisture during weighing.

Washing-soda and pearl-ash may be treated by a similar method to that described above.[2]

§ 30. Back Titrations [3]--Calcium Carbonate.

Suppose that whiting is to be investigated. Weigh out exactly 1 grm. of the dried (110°) sample on a piece of black glazed paper.[4] Brush [5] every trace of powder from the paper into a dry 400 c.c. flask. Take care that no powder sticks to the neck of the flask and so escapes the subsequent action of the

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[1] In that case we should have to use a 100 c.c. burette, or a normal solution. If 1·325 grms. of powder be weighed, $2n$ will represent the percentage amount of Na_2CO_3 in the sample.

[2] See page 60 *et seq.* for a more detailed analysis of soda ash.

[3] F. Mohr, *Liebig's Ann.*, 86, 129, 1853.

[4] Cut into the form of an elongated ∇. The narrow end is not too wide to pass into the neck of the flask. The paper is folded lengthwise so as to form a kind of gutter. The powder is placed near the broad end, and the narrow end of the paper is placed in the neck of the flask. The flask is then placed upright and the powder is transferred to it by tapping and brushing.

[5] Good camel-hair brushes, with the hair cut rather shorter than the brushes used by painters, are convenient for this purpose. A selected tail-feather of the *Gallus domesticus*
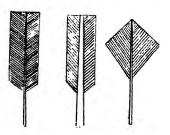
FIG. 20.—Dust Brushes.

(barnyard fowl), trimmed as indicated in fig. 20, is usually more effective than the brush. The brushes and feathers are best kept in a glass box.

acid.[1] Alternatively the sample can be weighed out on a watch-glass and transferred to the flask through a dry funnel. Any particles of the whiting adhering to the sides of the funnel and the watch-glass are rinsed into the flask. The funnel is removed and 50 c.c. of 1·0N-HCl pipetted into the flask. When all action has subsided, shake the flask vigorously. Add two drops of methyl orange [2] and titrate the solution with 1·0N-NaOH until the yellow colour of the methyl orange appears.[3]

The calculation is as follows:— Suppose that v c.c. of 1·0N-NaOH were taken to neutralise the acid remaining after the reaction. Then, since 1 c.c. of 1·0N-NaOH neutralises 1 c.c. of 1·0N-HCl, v c.c. of 1·0N-NaOH will neutralise v c.c. of 1·0N-HCl.

Hence,

$$\text{Volume of } 1\text{·}0\text{N-HCl taken} = 50\text{·}0 \text{ c.c.}$$
$$\text{Volume of } 1\text{·}0\text{N-HCl unused} = v \text{ c.c.}$$
$$\text{Volume of } 1\text{·}0\text{N-HCl reacting} = (50 - v) \text{ c.c.}$$

Thus 100 grms. of the sample will react with $(50 - v) \times 100$ c.c. of 1·0N-HCl or $(50 - v) \times 100 \times 0\text{·}0365 = 3\text{·}65(50 - v)$ grms. of HCl.

From the equation

$$CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2$$

it follows that $2 \times 36\text{·}5$ grms. of HCl react with 100·08 grms. of $CaCO_3$, hence $3\text{·}65 \times (50 - v)$ grms. of HCl will react with $[3\text{·}65 \times (50 - v) \times 100\text{·}08]/(2 \times 36\text{·}5)$ $= 5\text{·}004 \ (50 - v)$ grms. of $CaCO_3$.

A similar method can be used for evaluating substances such as barium and magnesium carbonates, zinc and magnesium oxides. The method can also be used for determinations of the amount of calcium carbonate in samples of ground flint or stone, felspar and powdered chert. A given weight of these materials is treated with decinormal acid and alkali as indicated above. For instance, 5 grms. of flint (dried at 110°) were digested with 50 c.c. of 0·1N-HCl on a water-bath. The cold solution was titrated with 0·1N-NaOH. The mean of three experiments gave 39·51 c.c. of 0·1N-NaOH. Hence, $50 - 39\text{·}51 = 10\text{·}49$ c.c. of 0·1N-HCl reacted with the calcium carbonate in the flint. But 1000 c.c. of 0·1N-HCl correspond with 5·004 grms. of $CaCO_3$; hence, 10·49 c.c. correspond with 0·05249 grm. of $CaCO_3$ per 5 grms. of flint—that is, 1·05 per cent. $CaCO_3$. Summarising the arithmetic, it follows that the percentage

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[1] Erlenmeyer flasks (fig. 21 a) with a broad neck are recommended for titrations. The neck and bottom should be such as to permit easy cleaning with the "bottle brush" and

FIG. 21.—Modified Flasks.

"policeman," page 81. When liquids are effervescing or boiling, the neck should be stopped with a bulb made for the purpose, or a funnel. The stoppers are afterwards washed. To prevent loss by spurting, unsymmetrical Erlenmeyer flasks may be used, such as Bolton flasks (fig. 21 b and c) or Herzka's pattern (fig. 21 d and e). For divided flasks to counteract over-titration, see J. Lindner, *Chem. Ztg.*, **52**, 868, 1928; J. W. Young, *Ind. Eng. Chem. Anal. Ed.*, **6**, 388, 1934.

[2] If phenolphthalein be used as indicator, the solution must be boiled before the titration in order to get rid of the carbon dioxide in the solution.

[3] The "transition tint" is often taken as the end-point.

amount of $CaCO_3$ in the given sample is represented within a very small margin of error [1] by $(50 - v)/10$.

It will be observed that if $0\cdot01N$-NaOH had been used for the back titration with the idea of obtaining more exact results, *the "increased accuracy" would have been illusory*, for the accuracy of the process depends on the exactness of the measurement of the more concentrated solution.

§ 31. Back Titration—Mixed Hydroxides and Carbonates.

Suppose it be required to determine the amount of caustic soda in a given sample of soda ash.[2] Dissolve, say, 50 grms. in warm water, filter and wash the insoluble matter, if any be present.[3] Make the filtrate and washings up to 1 litre. Titrate 20 c.c., equivalent to 1 grm., as indicated above with $0\cdot5N$-acid and methyl orange as indicator. This titration includes sodium carbonate as well as caustic soda and sodium sulphide, if these be present. To determine the caustic soda, pipette, say, 40 c.c. into a 200 c.c. flask, add a slight excess [4] of barium chloride (20 c.c. of a 10 per cent. solution will suffice). Barium carbonate is precipitated. Make the liquid with the solid in suspension up to the mark

FIG. 22.—Measuring Liquids.

with cold distilled water. Shake the corked flask. When the solution is cold,[5] again make it up to the mark on the neck with cold distilled water. Shake

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[1] Since the molecular weight of calcium carbonate is $100\cdot08$, not 100, the actual figures are $(50 - r) \times 0\cdot10008$.

[2] Method due to C. Winkler. W. Poethke and P. Manicke, *Zeit. anal. Chem.*, **79**, 241, 1929; A. C. Andersen, *Tids. Kem. Farm. Terapi*, **11**, 161, 1908; *J. Pharm. Chim.*, **28**, 370, 1908; R. B. Warder, *Chem. News.* **43**, 228, 1881; P. L. Aslanoglou, *ib.*, **70**, 166, 1894; C. A. Seyler, *ib.*, **70**, 187, 1894; J. E. Clennell, *ib.*, **71**, 93, 1895; W. E. Ridenour, *ib.*, **84**, 202, 1901; G. Lunge and W. Lohhöfer, *Zeit. angew. Chem.*, **14**, 1125, 1901; G. Lunge, *ib.*, **10**, 169, 1897; J. Tillmans and O. Heublein, *ib.*, **24**, 874, 1911; A. Suchier, *ib.*, **44**, 534, 1931. (There is an error due to the escape of carbon dioxide obviated by the method indicated in the text.) F. W. Küster, *Zeit. anorg. Chem.*, **13**, 142, 1897; C. F. Cross and E. J. Bevan, *Zeit. anal. Chem.*, **37**, 685, 1898; K. Novotný, *Zeit. Elektrochem.*, **11**, 453, 1905; M. le Blanc and K. Novotný, *Zeit. anorg. Chem.*, **51**, 181, 1906; M. le Blanc, *ib.*, **53**, 344, 1907; F. W. Küster, *ib.*, **13**, 127, 1896; S. P. L. Sörensen, *Zeit. anal. Chem.*, **47**, 279, 1908; J. Lindner, *ib.*, **72**, 135, 1927; **78**, 188, 1929; H. Seger and E. Cramer, *Tonind. Ztg.*, **18**, 593, 1894; B. North and W. C. Lee, *Journ. Soc. Chem. Ind.*, **21**, 322, 1902; S. G. Simpson, *Ind. Eng. Chem.*, **16**, 709, 1924; J. E. S. Han, *ib. Anal. Ed.*, **6**, 209, 1934; J. E. S. Han and T. Y. Chao, *ib.*, **4**, 229, 1932.

[3] The amount can be determined by drying and weighing, if needed (page 133).

[4] According to W. Smith (*Journ. Soc. Chem. Ind.*, **1**, 85, 1882), if a large excess of barium chloride be used, some alkali will be lost by adsorption. Exact precipitation is necessary to secure accuracy. S. P. L. Sörensen, *Zeit. anal. Chem.*, **45**, 220, 1906; **47**, 279, 1908.

[5] A COOLING BOX, in cases like this, where speed is essential, will be found a great convenience. This can be made of wood lined with sheet lead or sheet copper, and provided with entrance and overflow pipes for the cold water. The flask or flasks to be cooled are placed in the box, and a current of water allowed to flow through the box. To prevent the flasks overturning, either a series of lead rings can be provided to fit on the necks of the flasks, or a shelf with sockets may be fitted to the box.

the flask. Either let the precipitate settle and pipette off 50 c.c. from the clear liquid, or filter a portion of the solution and take 50 c.c. from the filtrate.[1] The standard flask shown in fig. 22 will be found very convenient for withdrawing aliquot portions from, say, a litre of solution. It is an ordinary litre flask with a side tap sealed into it before graduation, as shown in the diagram. Titrate the 50 c.c. with, say, 0·1N-HCl, using methyl orange as indicator. Each cubic centimetre of the 0·1N-acid will represent 0·004 grm. of NaOH per 0·5 grm. of soda ash; or, otherwise, the percentage of NaOH in the soda ash is 0·8v, where v is the volume of 0·1N-HCl used to titrate the above 50 c.c. of solution.[2]

Sulphides in the presence of chlorides can be determined volumetrically by Lestelle's process,[3] in which 100 c.c. of a solution containing the equivalent of, say, 5 grms. of soda ash are titrated with an ammoniacal solution of silver nitrate,[4] until no black precipitate of silver sulphide—Ag_2S—is formed on adding another drop of the silver nitrate solution. To observe the end-point accurately, the solution is filtered towards the end of the titration,[5] which is then continued if necessary. It may be necessary to repeat the filtration a number of times. With the above proportions, 1 c.c. of the standard solution represents 0·1 per cent. of sodium sulphide in the given sample.[6]

Sulphites are determined by acidulating 100 c.c. of a solution containing the equivalent of 5 grms. of the sample with acetic acid. Add starch solution and titrate with a standard iodine solution[7] until the blue colour of "starch-iodide" is permanent. For every 1 c.c. of the silver solution used in the sulphide test, deduct 5·1(3) c.c. from the iodine solution used in the titration. Each c.c. of the iodine solution is equivalent to 0·001576 grm. Na_2SO_3 or 0·0315 per cent. Na_2SO_3.

Sodium sulphate is best determined gravimetrically as barium sulphate (page 703); sodium chloride is determined by Mohr's process (page 68); iron, by the permanganate process (page 180); and sodium silicate, by evaporation with hydrochloric acid (page 147).

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[1] According to A. Müller (*Journ. prakt. Chem.*, (1), 83, 384, 1861) the filter paper adsorbs an appreciable quantity of the barium salt, and gives low results. But here we are now only concerned with the sodium hydroxide.

[2] Sodium sulphide, if present, will be included in this result, and a deduction must be made after the sulphides have been determined.

[3] H. Lestelle, *Compt. rend.*, 55, 739, 1862.

[4] AMMONIACAL SILVER NITRATE.—Dissolve 13·8203 grms. of silver in pure nitric acid, add 250 c.c. of concentrated ammonia and dilute the solution to a litre. 1 c.c. represents 0·005 grm. Na_2S. The ammonia keeps the silver chloride in solution.

[5] Some recommend a Beale's tube for this purpose. A piece of filter-paper is tied over the lower end A, fig. 23, and a piece of muslin is tied over the paper to prevent it breaking. When

FIG. 23.—Beale's Filter Pipette.

the end A is dipped in the mixture, clear liquid rises in the cylinder. This is poured from the little spout B and tested. If the titration be not completed, the liquid withdrawn must be returned to the main solution.

[6] If no sulphites are present, the titration for sulphides is best made by the process used for sulphites as given in the next paragraph.

[7] IODINE SOLUTION: 3·173 grms. of iodine per litre, *i.e.* 0·025N. See page 287 for details—preparation and precautions.

§ 32. Correction for the Volume of Suspended Solids.

It is here necessary to examine the nature of the error due to the assumption that the solid barium carbonate in suspension occupies no appreciable volume. The error will obviously be negligibly small when the volume of the solid is small in comparison with the volume of the solution, but the error may be considerable when the volume of the precipitate is appreciable in comparison with the volume of the flask.[1] It is therefore necessary to look into this subject more closely.

By a previous titration we found the amount of sodium carbonate per 20 c.c. of solution, that is, per gram of soda ash; let the amount of sodium carbonate so found be a grms. One gram of sodium carbonate is equivalent to 1·862 grms. of barium carbonate. Hence, a grms. of sodium carbonate will be equivalent to $1·862a$ grms. of barium carbonate. The specific gravity of dry barium carbonate is 4·3. Hence, the volume of the barium carbonate will be $0·433a$ c.c. If the soda ash contained 98 per cent. of sodium carbonate, $a = 0·98$. Thus the barium carbonate produced by the precipitation of the sodium carbonate in one gram of the soda ash (or 20 c.c. of the solution) will occupy $0·433 \times 0·98 = 0·424$ c.c. Now in the determination of the caustic soda in the soda ash, 40 c.c. of solution were taken and, after precipitation of the carbonate, the solution and suspended solid were made up to 200 c.c. Hence, the actual volume of the liquid was not 200 c.c. but $200 - (2 \times 0·424) = 199·152$ c.c. By drawing off 50 c.c. for the titration we drew, not the equivalent of 0·5 grm., but of 0·5021 grm. Consequently, each c.c. of the 0·1N-acid represented 0·004 grm. of NaOH per 0·5021 grm. of soda ash, *i.e.* the percentage of sodium hydroxide in the soda ash becomes $0·7966v$ instead of $0·8v$ (see page 61). The error may be somewhat serious when appreciable amounts of NaOH are in question, although the correction is usually neglected in practice.[2]

The process just indicated may be a little more complicated. In determining soluble sulphates, a known amount of barium chloride may be added to the slightly acidified solution. The solution is boiled to get rid of carbon dioxide and then exactly neutralised. An excess of a standard solution of sodium carbonate is then added. The solution is made up to a definite volume and the excess of sodium carbonate in an aliquot portion of the clear liquid titrated with standard acid. This gives data sufficient to calculate the amount of barium chloride which reacted with the sodium carbonate. The remaining barium chloride must have reacted with the soluble sulphates. We have both barium sulphate and barium carbonate in suspension. For the sake of illustration, assume that it is required to calculate the amount of barium chloride in a given solution. Add an excess of sodium carbonate, say, N or 1000 mgrms. (*i.e.* 1 grm.), and make the solution with the precipitate in suspension up to the

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[1] O. Eberhard, *Zeit. öffent. Chem.*, **4**, 867, 1898; M. Ruoss, *Zeit. anal. Chem.*, **37**, 422, 1898; M. Bicard and H. Pellet, *Zeit. anal. Chem.*, **24**, 460, 1885; *Bull. Assoc. Chim. Suc.*, **1**, 230, 1885; E. Lenoble, *Bull. Soc. chim.*, (3), **11**, 336, 1895; W. R. Smith, *Journ. Amer. Chem. Soc.*, **31**, 935, 1909; H. D. Steenbergen, *Chem. Weekb.*, **15**, 1268, 1918. In the previous determination advantage may be taken of the fact that dilute solutions of oxalic acid exert no appreciable action on alkaline earth carbonates, to titrate with standard oxalic acid all the liquid with the precipitate instead of an aliquot portion. Phenolphthalein as indicator.

[2] Say, checking the composition of black ash; *vide* G. Lunge, *Journ. Soc. Chem. Ind.*, **9**, 1013, 1890. The neglect may be sometimes justified when comparable results are alone required. In some cases the error might even be greater than the percentage amount of the constituent in question. A different method of analysis, of course, is then used.

V c.c. mark in a standard flask, say, $V = 50$ c.c. Either pipette or filter v c.c. of the clear solution, suppose $v = 25$ c.c. The sodium carbonate is determined by titration with standard acid. Suppose that 22·35 c.c. of 0·2N-acid are needed. Hence, 50 c.c. needed $22\cdot35 \times 2 = 44\cdot7$ c.c. of 0·2N-acid; then the excess of sodium carbonate, w, was $44\cdot7 \times 10\cdot6 = 473\cdot8$ mgrms. Thus the amount of sodium carbonate reacting with the barium chloride is $1000 - 473\cdot8 = 526\cdot2$ mgrms. But 1 grm. of sodium carbonate is equivalent to 1·862 grms. of barium carbonate, consequently 526·2 mgrms. of sodium carbonate will represent $1\cdot862 \times 526\cdot2 = 979\cdot8$ mgrms., say a mgrms., of barium carbonate, or

$$a = 1\cdot862(1000 - w) \qquad . \qquad . \qquad . \qquad (1)$$

This number $a = 979\cdot8$ mgrms. is not quite right, because we did not allow for the volume of the precipitate. Let A be the right value which would have been obtained had the precipitate been filtered off, washed, and the filtrate and washings made up to V c.c. Then,

$$A = 1\cdot862(1000 - W) \qquad . \qquad . \qquad . \qquad (2)$$

where W represents the correct excess of sodium carbonate which would have been obtained in the filtrate if the precipitate had occupied a negligibly small volume. Let s denote the specific gravity of the precipitate (sp. gr. $BaCO_3$ $= 4\cdot3$). The precipitate then occupies $A/1000s$ c.c. Hence $(V - A/1000s)$ c.c. of solution actually contain w grms. of sodium carbonate, whereas if the precipitate had occupied a negligible volume, this weight of sodium carbonate would have been contained in V c.c. Thus

$$W = w(V - A/1000s)/V \quad \text{or} \quad w - W = wA/1000sV$$

The error is, then, from (1) and (2),

$$A - a = 1\cdot862(w - W) = 1\cdot862Aw/1000sV$$

Consequently

$$A = \frac{1000sVa}{1000sV - 1\cdot862w}$$

Substituting this value for A on the right-hand side of (3) we get:

$$A - a = \frac{1\cdot862aw}{1000sV - 1\cdot862w}$$

The term $1\cdot862w$ in the denominator is very small in comparison with $1000sV$, so that it can be omitted without materially affecting the value of the fraction. Hence, the error

$$A - a = \frac{1\cdot862 \times 979\cdot8 \times 473\cdot8}{1000 \times 4\cdot3 \times 50} = 4\cdot0 \text{ mgrms.}$$

Thus the total weight of the barium carbonate is $979\cdot8 + 4\cdot0 = 983\cdot8$ mgrms. The amount of barium chloride corresponding with this barium carbonate is readily calculated. All this arithmetic may be summarised in the formula:

$$\text{Weight of precipitate} = r(N - w)\left(1 + \frac{w}{1000sV}\right) \qquad . \qquad . \qquad (4)$$

where N denotes the weight of the precipitating agent in mgrms. (1000); s, the specific gravity of the precipitate (4·3); V, the volume of the measuring flask (50); w, the excess of the precipitating agent (473·8); and r, the ratio of the equivalent weight of the precipitate and precipitating agent ($98\cdot68 \div 53\cdot00 = 1\cdot862$). A great many "rapid" processes involve the use of one or other of these two methods of correction. Once the reasoning is understood, there is

no need to go through all the steps. The numbers corresponding with the letters can be substituted directly in formula (4).[1]

§ 33. Sodium Silicate—Water-Glass.

In commercial water-glass—sodium silicate—the ratio $SiO_2 : Na_2O$ generally lies between 2 : 1 and 4 : 1. In analysis, it is generally assumed [2] that free caustic alkali is present when this ratio falls below 1 : 1, corresponding with about 50·8 per cent. of Na_2O, or with $Na_2O.SiO_2$. Water-glass is found on the market in the form of a solid yellowish or greenish glass, or in a more or less viscid aqueous solution.

For analysis, 10 grms. of the solid are ground to a very fine powder and dissolved in hot water,[3] or 20 grms. of the liquid are digested in water. In both cases the solution is made up to 500 c.c. It may be necessary to let the solution stand some time in order to allow the insoluble matter to settle as a sediment.[4]

1. *Combined and Free Alkali.*[5]—Titrate 100 c.c. of the clear solution with N- or 0·5N-HCl, using phenolphthalein as indicator. The action of the acid is represented by the equation

$$Na_2SiO_3 + 2HCl = 2NaCl + H_2SiO_3$$

The liberated silicic acid does not affect the indicator. The reaction towards the end is very slow and the indicator may appear to be permanently de-colorised before the reaction is complete. There is therefore some danger of under-titration. If, however, a large excess of sodium chloride be added before the titration, this difficulty does not give much trouble.[6] From the preceding equation, we see that every c.c. of N-hydrochloric acid corresponds with 0·031 grm. of Na_2O. Hence, if w grms. of the sample were made up to 500 c.c., and if v c.c. of the N-hydrochloric acid were used in titrating 100 c.c. of the solution, the sample has $0·155v$ grm. of Na_2O per w grms. of sample.

2. *Free Alkali.*—To 100 c.c. of the solution,[7] add 100 c.c. of a solution of 10 grms. crystalline barium chloride gradually with constant stirring. Make the solution up to 250 c.c. Shake well. Filter through dry filter-paper. Reject the first 20–30 c.c., and titrate the next 100 c.c. which passes through the paper with 0·1N-hydrochloric acid and phenolphthalein.[8] Since 1 c.c. of 0·1N-hydrochloric acid corresponds with 0·0031 grm. of Na_2O, if n c.c. of this acid are used in the titration, $n \times 0·0031$ grm. of Na_2O is present in 100 c.c. Hence, $n \times 0·0031 \times 2·5 = 0·00775n$ grm. of Na_2O is present in the 250 c.c. Hence, the sample has $0·03875n$ grm. of Na_2O per w grms. of the sample taken.

[1] It is also possible to compute the volume of the solid matter in suspension by an application of the principle indicated in § 32, page 62.

[2] There are some reasons for doubting if the assumption is valid.

[3] Some samples of water-glass dissolve only with great difficulty.

[4] The sediment can be filtered off, washed and determined later. J. Ordway, *Chem. News*, 9, 61, 1864.

[5] The term "combined alkali" does not here include the alkali which may be present in the form of neutral salts—*e.g.* sodium chloride. There is usually so little sediment that the correction indicated on page 62 is not needed.

[6] R. T. Thomson, *Chem. News*, 47, 135, 1883; C. Lunge and W. T. Lohöfer, *Zeit. angew. Chem.*, 14, 1125, 1901.

[7] The solution should be as concentrated as possible. Hence, some prefer to take 10 grms. made up to 100 c.c. for this determination.

[8] P. Heermann, *Chem. Ztg.*, 28, 883, 1904. If sodium carbonate be present, it will be precipitated as barium carbonate by the barium chloride.

The difference between the results of this and the preceding titration represents the amount of combined alkali.[1]

Calculation.—Suppose that 10 grms. of the powder were made up to 500 c.c. and that 21·2 c.c. of N-hydrochloric acid were needed for the first titration, and 1·85 c.c. of 0·1N-hydrochloric acid for the second titration. The results are expressed:—

Free alkali	0·72 per cent.
Combined alkali	32·14 ,,
Silica	63·81 ,,
Alkali chlorides, etc.	..
Insoluble matter	..
Water (loss on ignition, page 136) . . .	..

The basicity[2] of the sample, that is, the ratio $SiO_2 : Na_2O$, or the molecular proportion of the silica to the free and combined alkalies, regarded as soda, is $(63\cdot81 \div 60)/(32\cdot86 \div 62) = 2\cdot01$.

§ 34. The Volumetric Determination of Chlorine and Silver— Volhard's Process.

When potassium or ammonium thiocyanate is added to a solution of silver nitrate, a white precipitate of silver thiocyanate is formed:

$$AgNO_3 + NH_4CNS = AgCNS + NH_4NO_3$$

The precipitate is insoluble in nitric acid. The reaction occurs even in presence of ferric salts, and only when all the silver has been precipitated does the thiocyanate react with the ferric salt, forming the characteristic blood-red colour of ferric thiocyanate. The persistent appearance of this coloration shows that the titration is finished. Ferric nitrate or sulphate can be used as indicator, but not the chloride. Similarly, the water and other reagents must be free from chlorides.[3] This method is due to Charpentier, but usually called Volhard's process.[4]

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[1] The term "alkali" used here is supposed to represent soda, but potash may be present. If a distinction is necessary, a special analysis may be needed to determine the ratio $K_2O : Na_2O$. The silica is determined by evaporating 100 c.c. with hydrochloric acid, as indicated on page 147. The filtrate is treated with ammonia, ammonium carbonate and ammonium oxalate. Filter. The filtrate is evaporated with hydrochloric acid, ignited to drive off ammonium salts and the residue is supposed to represent the "alkalies." See page 220 for details. The "total alkalies" so obtained, less the free and combined alkalies, are regarded as alkali belonging to the neutral salts, *e.g.* alkali chloride. For the determination of silica in water-glass, see F. S. Pertschik, *Zeit. anal. Chem.*, **94**, 23, 1933; S. S. Korol and V. M. Koluzhskaya, *Zavodskaya Lab.*, **3**, 908, 1934.

[2] The term "acidity" might perhaps be more appropriately applied for the ratio $SiO_2 : Na_2O$.

[3] Chlorides interfere not only by removing silver as insoluble chloride, but they also interfere with the end-point, since silver chloride removes part of the red ferric thiocyanate from the solution.

[4] J. Volhard, *Journ. prakt. Chem.*, (2), **9**, 217, 1874; *Liebig's Ann.*, **190**, 1, 1878; *Zeit. anal. Chem.*, **13**, 171, 1874; **17**, 482, 1878; J. B. Schober, *ib.*, **17**, 467, 1878; G. Brügelmann, *ib.*, **16**, 1, 1877; I. M. Kolthoff, *ib.*, **56**, 568, 1917; M. B. Shchigol, *ib.*, **91**, 182, 1932; F. A. Falk, *Ber.*, **8**, 12, 1875; B. G. Gentil, *Wochenschr. Pharm.*, **30**, 133, 1903; P. Charpentier, *Bull. Soc. Ing. Civ. France*, 325, 1870; E. Drechsel, *Journ. prakt. Chem.*, (2), **15**, 191, 1877; C. Mann, *Oester. Zeit. Berg. Hütt.*, **26**, 426, 1878; H. F. von Jüptner, *ib.*, **28**, 33, 51, 1880; O. Lindemann, *Berg. Hütt. Ztg.*, **35**, 333, 1877; L. A. Congdon *et al.*, *Chem. News*, **129**, 302, 317, 334, 1924; F. T. Shutt and H. W. Charlton, *ib.*, **94**, 258, 1906; *Trans. Roy. Soc. Canada*, **11**, 67, 1906; A. Dubosc, *Ann. Chim. Anal.*, **9**, 45, 1904; C. Hoitsema, *Zeit. angew. Chem.*, **17**, 647, 1904; V. Rothmund and A. Burgstaller, *Zeit. anorg. Chem.*, **63**, 330, 1909; E. M. Hamilton, *Min. Scientific Press*, **102**, 364, 1911; A. T. Stuart, *Journ. Amer. Chem. Soc.*, **33**, 1344, 1911; A. E. Knorr, *ib.*, **19**, 814, 1897; J. V. Lawrence and J. A. Harris, *ib.*, **46**,

Standardisation of the Solutions.—A standard solution of, say, 0·1N-silver nitrate is made by dissolving 16·9888 grms. of pure silver nitrate [1] in water, and making the solution up to a litre with distilled water at 15°. A solution of potassium thiocyanate is made by dissolving 10 grms. of the salt in water and making the solution up to a litre.[2] This latter solution is standardised by pipetting, say, 25 c.c. of the silver nitrate solution into a white porcelain dish [3] and acidifying with a moderate excess of dilute nitric acid. Run the potassium thiocyanate solution from the burette until most of the silver is precipitated [4] as white silver thiocyanate, AgCNS, and then add about 5 c.c. of solution of ferric alum [5] to act as indicator. Each drop of the thiocyanate solution produces a white cloud of silver thiocyanate coloured with a reddish halo of ferric thiocyanate. The colour disappears on shaking, provided any silver nitrate remains in the solution. When all the silver has been precipitated as insoluble silver thiocyanate, one drop of the potassium thiocyanate will colour the solution reddish-brown. The colour persists after a vigorous shaking. The reddish-brown colour produced when the titration is not quite finished is but slowly removed when the solution is vigorously agitated. Hence it is necessary to guard against "under-titration." [6]

Suppose that 24·3 c.c. of the potassium thiocyanate solution are needed for the titration, it follows that 24·3 c.c. of this solution correspond with 25 c.c. of silver nitrate. If the potassium thiocyanate is to be exactly 0·1 normal, the 24·3 c.c. must be diluted to 25 c.c. Hence, proceed as indicated on page 39.

Determination of Silver.—The titration of the nitric acid solution of the sample [7] under investigation is conducted in the same way as that described for the standardisation of the potassium thiocyanate solution. The method is valuable provided an accuracy of 0·1 per cent. will suffice. The results are a little low when large quantities of silver are present, owing possibly to (1) the adsorption of some of the silver nitrate by the precipitated silver thiocyanate; and (2) the action of the precipitate on the solution. The process can also be

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1471, 1924; T. K. Rose, *Journ. Chem. Soc.*, **77**, 232, 1900; A. B. Keys, *ib.*, 2440, 1931; Y. N. Ivanov, *Journ. Russ. Phys. Chem. Soc.*, **45**, 66, 1913; *Chem. Ztg.*, **37**, 427, 1913; C. T. Hirst and J. E. Greaves, *Soil Sci.*, **9**, 41, 1920; B. van der Brug and C. A. Koppejan, *Chem. Weekb.*, **21**, 66, 167, 1924; I. M. Kolthoff and O. Tomiček, *ib.*, **21**, 106, 124, 1924; I. M. Kolthoff, *ib.*, **21**, 188, 1924; J. R. Caldwell and H. V. Moyer, *Ind. Eng. Chem. Anal. Ed.*, **7**, 38, 1935; I. M. Kolthoff and J. J. Lingane, *Journ. Amer. Chem. Soc.*, **57**, 2126, 1935.

[1] Powdered and dried at 130° for about an hour. The silver nitrate solution may also be prepared by dissolving 10·788 grms. of pure metallic silver in 50 c.c. of dilute nitric acid. Boil off the nitrous fumes, since they interfere with the indicator later on. Dilute the solution to a litre.

[2] It is very difficult to weigh out an exact quantity of potassium thiocyanate, owing to its deliquescent character. Hence the solution must be standardised. If a solution of definite strength be needed it is best to take rather more salt than is necessary and, when the strength of the solution has been determined, dilute the solution as indicated on page 39. However, for the use of potassium thiocyanate as a primary standard, see I. M. Kolthoff and J. J. Lingane, *Journ. Amer. Chem. Soc.*, **57**, 2126, 1935. For the stability of solutions of potassium thiocyanate, see E. N. Taran, *Journ. Gen. Chem., U.S.S.R.*, **5**, 602, 1935; F. H. Campbell and G. R. Hook, *Proc. Soc. Chem. Ind. Victoria*, **36**, 1106, 1936.

[3] Or in an Erlenmeyer flask or beaker, and then titrate with a white background as described on page 49.

[4] The results are low if the temperature be much higher than 25°. The nitric acid then "bleaches" the ferric thiocyanate. Sufficient nitric acid should be present to remove the colour produced by the indicator before the titration is finished. An excess of nitric acid does no particular harm, but a large excess gives low results since it retards the formation of the ferric thiocyanate at the end of the titration.

[5] FERRIC ALUM SOLUTION—Dissolve 10 grms. of ferric alum in 90 c.c. of water.

[6] In case of "over-titration" a known volume of the standard silver nitrate solution can be added to the solution and the titration continued. Due allowance must, of course, be made for the additional silver.   [7] For example, a silver coin, dissolved in nitric acid.

used in the presence of barium, bismuth, antimony, arsenic, lead, iron, manganese and zinc. Mercury interferes with the titration, since it is precipitated by the thiocyanate. Copper, cobalt and nickel form coloured solutions and thus interfere with the indicator, although it is claimed that 70 per cent. of copper will not spoil the determination.

Silver, in acid solution, can also be determined by direct titration with a standard solution of potassium iodide [1] or potassium bromide.[2]

Determination of Chlorides.—By this method silver can be determined in the presence of nitric acid, whereas Mohr's chromate process requires a neutral solution. Hence, the thiocyanate process can be used to determine the halides —chlorine, bromine and iodine—in the presence of phosphates and other salts which give precipitates with silver in neutral solutions, but not in acid solutions. Chlorides, bromides and iodides in solution are determined by adding an excess of a standard solution of silver nitrate. The excess of silver which has not reacted to form silver chloride is determined by titration with the standard thiocyanate.[3] Thus, W. Dittmar determined chlorides in sea-water by precipitating the chloride with an excess of standard silver nitrate, filtering off the silver chloride and titrating the excess of silver nitrate as indicated above.

It is important to filter off [4] the precipitate of silver chloride,[5] owing to the fact that the silver chloride reacts with the soluble thiocyanate so that 165 times as much excess 0·1N-ammonium thiocyanate per 200 c.c. is needed to produce the red coloration in the presence of silver chloride as is needed when the chloride is absent.[6] The results in the presence of the precipitated chloride are more variable and some 2 per cent. low under conditions where the results in the absence of the precipitated chloride are satisfactorily constant, and but 0·15 per cent. high when the silver chloride has been filtered off.[7] The presence of sulphates interferes with Volhard's process, because appreciable quantities of silver sulphate are precipitated with the chloride and thiocyanate.[8]

EXAMPLE.—An aliquot portion, say 20 c.c., of the solution of soda ash indicated on page 60, or an aqueous solution of a gram of the dry salt, is treated with an excess of nitric acid. Then add an excess, say 25 c.c., of 0·1N-silver nitrate solution, and titrate with 0·1N-potassium thiocyanate solution as indicated above. Suppose that 24·2 c.c. of the 0·1N-potassium thiocyanate solution are needed. This is equivalent to

[1] L. Schneider (*Journ. Amer. Chem. Soc.*, **40**, 583, 1918) uses palladous nitrate as internal indicator; P. Fleury and J. Courtois (*Bull. Soc. chim.*, (4), **49**, 860, 1931), starch-iodine; C. S. Shapiro (*Journ. Lab. Clin. Med.*, **20**, 195, 1934), starch; A. Bloom (*Ind. Eng. Chem. Anal. Ed.*, **8**, 167, 1936), a ceric salt and starch.

[2] A. J. Berry, *Analyst*, **61**, 315, 1936. Tartrazine or phenosafranine are used as adsorption indicators (see page 71).

[3] For iodides, the nitric acid is added after the standard silver solution.

[4] Say, in a filter tube containing glass-wool (page 89).

[5] M. A. Rosanoff and A. E. Hill, *Journ. Amer. Chem. Soc.*, **29**, 269, 1407, 1907; *Chem. News*, **96**, 264, 274, 299, 1907; G. A. Sanger, *Proc. Amer. Acad.*, **26**, 34, 1879; G. Brügelmann, *Zeit. anal. Chem.*, **16**, 1, 1877; E. Drechsel, *ib.*, **16**, 351, 1877; *Journ. prakt. Chem.*, (2), **15**, 191, 1877; O. Knüpfer, *Zeit. phys. Chem.*, **25**, 266, 1898; L. L. de Koninck, *Chem. Ztg.*, **15**, 1558, 1891; L. A. Congdon *et al.*, *Chem. News*, **129**, 302, 317, 334, 1924. Instead of filtering off the precipitated chloride, V. Rothmund and A. Burgstaller (*Zeit. anorg. Chem.*, **63**, 330, 1909) coagulate it by adding sufficient ether to form two layers, and then finish the titration. Alternatively, M. B. Shchigol (*Zeit. anal. Chem.*, **91**, 182, 1932) adds 5–10 c.c. of benzene, toluene or xylene before precipitation, while J. R. Caldwell and H. V. Moyer (*Ind. Eng. Chem. Anal. Ed.*, **7**, 38, 1935) recommend the addition of 1 c.c. of nitrobenzene for each 0·05 grm. of chloride in solution.

[6] With bromides and iodides, the interference of the precipitated salt is negligibly small, owing to the much lower solubilities of silver bromide and iodide in water.

[7] A. B. Keys (*Journ. Chem. Soc.*, 2440, 1931) has described a micro-modification of the Volhard process which is stated to give an accuracy of the order of 0·001 mgrm. of chlorine.

[8] L. W. Andrews, *Journ. Amer. Chem. Soc.*, **29**, 275, 1907.

24·2 c.c. of the silver nitrate solution. Hence, $25 - 24 \cdot 2 = 0 \cdot 8$ c.c. of the silver nitrate solution has formed silver chloride. But 1 c.c. of 0·1N-silver nitrate solution will react with 1 c.c. of 0·1N-sodium chloride solution, i.e. 0·0058454 grm. of sodium chloride. Thus the solution contains $0 \cdot 8 \times 0 \cdot 0058454 = 0 \cdot 0047$ grm. of sodium chloride. Hence, the sample has the equivalent of 0·47 per cent. of sodium chloride.

§ 35. The Volumetric Determination of Chlorides—Mohr's Chromate Process.

If a solution of silver nitrate be gradually added to a neutral solution of an alkali chloride containing a little potassium chromate, silver chloride will be precipitated. The reaction is represented by the equation:

$$AgNO_3 + KCl = AgCl + KNO_3$$

When the reaction is complete, any further addition of the silver nitrate reacts with the potassium chromate:

$$2AgNO_3 + K_2CrO_4 = Ag_2CrO_4 + 2KNO_3$$

The permanent red tint of the silver chromate so developed indicates that the reaction between the silver nitrate and the alkali chloride is at an end. The reaction is quantitative and was used by Mohr for the volumetric determination of chlorides [1] by using a standard solution of silver nitrate.

If acids be present, the chromate may form dichromate, which interferes with the recognition of the end-point and, moreover, acids dissolve appreciable quantities of the silver chromate, and the end-point is then indistinct. Hence, any acids which may be present should be neutralised by sodium carbonate, or, better, by pure calcium carbonate.[2] If the solution be feebly alkaline, owing to the presence of a slight excess of carbonate, a little silver carbonate will be precipitated with the chromate. Alkaline solutions should accordingly be neutralised with acetic or nitric acid. A slight alkalinity is not so baneful as a slight acidity.

The Titration.—Dissolve a gram of the dried sample under investigation in water and make the solution up to 100 c.c. Pipette 25 c.c. into an Erlenmeyer flask and add 1 c.c. of potassium chromate solution.[3] Gradually add 0·1N-silver nitrate solution [4] with constant stirring or agitation. When the chloride

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[1] F. Mohr, *Liebig's Ann.*, **97**, 335, 1856. Mohr first used potassium arsenate as indicator; A. Levol (*Bull. Soc. Encour.*, **52**, 220, 1853; *Journ. prakt. Chem.*, (1), **60**, 384, 1853) used sodium phosphate; F. Stolba (*Zeit. anal. Chem.*, **13**, 65, 1874), potassium calcium chromate. See B. M. Margosches, *Zeit. anorg. Chem.*, **41**, 68, 1904; L. L. de Koninck and E. Nihoul, *Zeit. angew. Chem.*, **4**, 295, 1891; M. Lombard, *Bull. Soc. chim.*, (4), **13**, 1006, 1913; 1. M. Kolthoff, *Pharm. Weekb.*, **54**, 612, 1917; L. A. Congdon *et al.*, *Chem. News*, **129**, 302, 317, 334, 1924; I. M. Kolthoff and L. H. van Berk, *Zeit. anal. Chem.*, **70**, 369, 1927; A. J. Mee, *Chem. and Ind.*, 520, 1933.

[2] H. W. Doughty (*Journ. Amer. Chem. Soc.*, **46**, 2707, 1924) says that chlorides can be titrated in any acid solution by Mohr's process, provided the p_H value of the solution is reduced to 5–7 by the addition of a buffer mixture of sodium acetate (2 mols.) and acetic acid (1 mol.).

[3] POTASSIUM CHROMATE SOLUTION.—Dissolve 1 grm. of the salt in 100 c.c. of water. The chromate must be free from chlorides. To test for chlorides, dissolve the chromate in water, add a little silver nitrate and then some nitric acid. If the red precipitate which forms dissolves completely, forming a clear solution, chlorides are absent.

[4] SILVER NITRATE SOLUTION.—Dissolve 16·9888 grms. of pure silver nitrate in a litre of water. 1 c.c. corresponds with 0·003547 grm. of chlorine. If this solution be standardised by dissolving 5·8454 grms. of pure sodium chloride in a litre of water, so as to form a 0·1N-sodium chloride solution, 25 c.c. of the 0·1N-sodium chloride will require 25·1 c.c. instead of 25 c.c. of the 0·1N-silver nitrate solution. E. N. Taran (*Journ. App. Chem., U.S.S.R.*, **9**, 520, 1936) standardises silver solutions by boiling an aliquot portion of the solution with a slight excess of formaldehyde in 15 per cent. ammonia. The precipitated silver is ignited at 450°–500° to drive off adsorbed substances.

is all precipitated a red coloration of silver chromate will appear which does not disappear on agitation of the solution. The silver nitrate must be added very slowly towards the end of the titration, so as to run no risk of over-titration. The titration is made with the flask over a sheet of white paper, or a white tile.

A certain amount of silver nitrate is needed to colour the indicator. Hence, Mohr recommends adding, drop by drop, 0·1N-sodium chloride solution until the red colour of the indicator gives way to the yellow colour of the alkali chromate. Deduct the volume of sodium chloride so used from the silver nitrate used in the titration. The result represents the amount of silver nitrate corresponding with the chlorides undergoing titration.

If the precipitate of silver chloride is very large, the end-point will be somewhat masked.[1] In that case, add a slight excess, 1–2 c.c., of a dilute standard solution of (0·1N) sodium chloride. Filter and wash the precipitate twice with water, and again titrate the clear solution, making allowance for the extra sodium chloride added.

Disturbing Agents.—Salts of lead, bismuth, barium and iron will form insoluble chromates and should therefore be absent;[2] coloured salts—cobalt, nickel, and copper—obscure the end-point and are therefore objectionable. Pellet[3] has shown that arsenates, arsenites, phosphates and fluorides do not interfere, since silver chromate forms earlier than the silver salts of these acids.

The presence of any salt which augments the solubility of the silver chromate gives high results, since more silver nitrate must be added to produce the red chromate than corresponds with the end of the reaction. Hence, for instance, the nitrates of the alkalies and alkaline earths[4] and ammonium salts should be absent. The solubility of the silver chromate is also augmented by raising the temperature of the solution[5] and, in consequence, it is best to titrate cold solutions. An excess of potassium chromate diminishes the solubility of the silver chromate and, in consequence, a larger quantity of the indicator is used than would normally be the case If too little potassium chromate be used, more silver nitrate is needed to produce the red-coloured chromate.[6]

Difficulty with the Indicator.—In spite of these precautions, a measurable excess of silver nitrate solution must be added after the reaction with the chlorides is ended, before the permanent red colour of the silver chromate is developed. This is particularly noticeable when small quantities of chloride are present in large volumes of solution, and Winkler[7] has accordingly drawn up an empirical correction table (Table XII.) representing the excess of silver nitrate solution (1 c.c. equivalent to 0·001 grm. chlorine) needed to develop

[1] With strong solutions of the chlorides of the alkali metals, magnesium and calcium, A. Lottermoser and W. Lorenz (*Kolloid Zeit.*, 68, 201, 1934) find that the addition of 5–10 c.c. of agar solution before titration prevents the coagulation of the precipitated silver chloride. A sharp end-point is then given with accurate and reproducible results.

[2] With chlorides of metals which give chromates less soluble than silver chromate, H. W. Bolam (*Chem. News*, 120, 292, 1920) adds slightly more potassium chromate than is necessary to precipitate the chromate of the metal and then proceeds as usual.

[3] H. Pellet, *Bull. Soc. chim.*, (2), 28, 68, 1877.

[4] F. C. Carpenter, *Journ. Soc. Chem. Ind.*, 5, 286, 1886—sodium and calcium nitrates have least effect; ammonium, potassium and magnesium the greatest effect. G. Biscaro, *Chem. News*, 53, 67, 1886; *Ann. Chim. Med. Farm.*, (4), 1, 241, 1885; L. L. de Koninck and E. Nihoul, *Zeit. angew. Chem.*, 4, 295, 1891; H. Baubigny and Q. Chavanne, *Compt. rend.*, 136, 1197, 1903.

[5] A litre of water dissolves 0·0225 grm. of silver chromate at 14·8° and 0·084 grm. at 75°—F. Kohlrausch, *Zeit. phys. Chem.*, 64, 121, 1908. See also G. S. Whitby, *Zeit. anorg. Chem.*, 67, 107, 1910.

[6] L. L. de Koninck and E. Nihoul, *Rev. Univ. Mines*, (3), 16, 42, 1891; *Zeit. angew. Chem.*, 4, 295, 1891.

[7] L. W. Winkler, *Zeit. anal. Chem.*, 40, 596, 1901.

the colour of the indicator in 100 c.c. of solution, when 1 c.c. of a one per cent. solution of potassium chromate is used.

Table XII.—Correction for Indicator in Mohr's Chromate Process for Chlorides.

Silver solution used.	Deduction.	Silver solution used.	Deduction.	Silver solution used.	Deduction.
c.c.	c.c.	c.c.	c.c.	c.c.	c.c.
0·2	0·20	0·8	0·39	5·0	0·50
0·3	0·25	0·9	0·40	6·0	0·52
0·4	0·30	1·0	0·41	7·0	0·54
0·5	0·33	2·0	0·44	8·0	0·56
0·6	0·36	3·0	0·46	9·0	0·58
0·7	0·38	4·0	0·48	10·0	0·60

Naturally this table refers only to solutions of the concentration stated. Lunge deducts 0·2 c.c. from the amount of 0·1N-silver nitrate solution used both in titrating a solution of sodium chloride which requires 50 c.c. of the standard solution, and in titrating sodium sulphate which contains a little sodium chloride. Winkler's experiments show that Lunge's correction is probably about right. Fresenius[1] recommends making the solution to be titrated approximately the same volume and strength as the solution used in standardising the silver solution. Hazen[2] recommends a deduction of $0.003V + 0.02$ c.c. from the standard silver solution, when V denotes the volume of the solution which has just been titrated.

If the correction be neglected when, say, a 0·1N-silver nitrate solution is used, the resulting error is about 0·4 per cent.[3]

Modification for Small Amounts of Chlorides.—When very small amounts of chlorides are in question, more dilute solutions of silver nitrate are used— say, 4·7914 grms. of silver nitrate per litre; 1 c.c. of this solution represents 0·001 grm. of chlorine; or 2·3957 grms. of silver nitrate per litre; 1 c.c. of this solution represents 0·0005 grm. of chlorine.[4] Suppose that the mixed chlorides obtained in the determination of the alkalies in clays be in question.[5] Add 1 c.c. of the potassium chromate solution. Make the solution up to 50 c.c. in an Erlenmeyer flask. Add 50 c.c. of distilled water to the same amount of potassium chromate solution in a similar flask; this is used for comparing with the contents of the flask which are being titrated, so that a change of colour of the indicator can be quickly detected. The correction for the amount of silver nitrate solution needed to colour the indicator can be made in the same flask.[6] The titration is made over a white porcelain tile or sheet of white paper. Use a

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[1] R. Fresenius, *Quantitative Analysis*, London, **1**, 356, 1876.

[2] A. Hazen, *Amer. Chem. Journ.*, **11**, 409, 1889.

[3] One c.c. of the silver solution corresponds with 0·0058454 grm. of sodium chloride. Lunge's correction, 0·2 c.c., corresponds with 0·0011691 grm. sodium chloride. If w grms. of the sample be in question, the percentage error will be equivalent to $0.11691/w$ per cent. of sodium chloride. If $w = 0.2923$ grm., the corresponding error will be 0·4 per cent.

[4] For the colorimetric determination of chlorides in water, see H. B. Riffenburg, *Ind. Eng. Chem. Anal. Ed.*, **7**, 14, 1935.

[5] G. Bruhns (*Zeit. angew. Chem.*, **31**, (1), 156, 1918) finds that chlorides can be titrated by Mohr's process in the presence of silica provided that the latter, if gelatinous, is in a finely divided state and the solution is made neutral to phenolphthalein with nitric acid.

[6] Or use Winkler's Table XII.

burette reading to $\frac{1}{20}$ths or $\frac{1}{50}$ths c.c. Yellow gaslight gives better results than daylight. Some prefer to work in a dark room with a yellow monochromatic light.[1]

Adsorption Indicators.—In 1923 Fajans and Hassel introduced the use of adsorption indicators into Mohr's process.[2] According to Kolthoff,[3] at or just beyond the equivalence point the precipitated silver halide adsorbs silver ions and the "silver body" so formed then adsorbs the indicator from the solution with the production of a highly coloured complex on the surface of the precipitate. The consensus of opinion is that such indicators give more accurate results than do alkali chromates, particularly in very dilute solutions and in the determination of small amounts of halides. Among the various substances which have been recommended as adsorption indicators,[4] dichlorofluorescein works admirably for the determination of chlorides.

The Titration.—If necessary, the chloride solution is diluted down to about 0·025 normal strength, and then two drops of indicator[5] are added per 10 c.c. of solution. On titration, the silver chloride remains in colloidal solution which towards the end-point has a yellowish-orange colour. When the end-point is nearly reached, the silver chloride coagulates. The standard silver solution is now added drop by drop until, at the end-point, the precipitate suddenly turns red. Titrations can be made accurately with standard silver solutions as dilute as 0·01 normal.[6]

[1] A. Dupré (*Analyst*, 5, 123, 1880) watches the progress of the titration through a flat glass cell, 1 centimetre thick, containing a solution of neutral potassium chromate of approximately the same tint as the solution undergoing titration. The latter appears to be a colourless liquid like water when observed through the cell and the first appearance of red is easily seen through the cell.

[2] K. Fajans and O. Hassel, *Zeit. Elektrochem.*, 29, 495, 1923; K. Fajans and H. Wolff, *Zeit. anorg. Chem.*, 137, 221, 1924; W. Bottger and K. O. Schmidt, *ib.*, 137, 246, 1924; I. M. Kolthoff and L. H. van Berk, *Zeit. anal. Chem.*, 70, 369, 1927; S. Malowan, *Chem. Ztg.*, 57, 76, 1933.

[3] I. M. Kolthoff, W. M. Lauer and C. J. Sunde, *Journ. Amer. Chem. Soc.*, 51, 3273, 1929; I. M. Kolthoff, *Kolloid Zeit.*, 68, 190, 1934; *Chem. Rev.*, 16, 87, 1935; K. Fajans in *Die Chemische Analyse*, Stuttgart, 33, 161, 1935.

[4] A. J. Berry and P. T. Durrant, *Analyst*, 55, 613, 1930; A. J. Berry, *ib.*, 57, 511, 1932; H. R. Fleck, R. F. G. Holness and A. M. Ward, *ib.*, 60, 32, 1935; N. P. Rudenko, *Journ. Russ. Phys. Chem. Soc.*, 62, 505, 1930; L. Belladen and G. Piazza, *Ann. Chim. appl.*, 22, 631, 1932; Y. Uzumasa and Y. Miyake, *Journ. Chem. Soc. Japan*, 53, 904, 1932; 54, 1043, 1933; 55, 627, 1934; E. J. Kocsis and L. Pollak, *Magyar Chem. Fol.*, 40, 99, 1934; E. J. Kocsis, *Zeit. anorg. Chem.*, 221, 318, 1935; K. Bambach and T. H. Rider, *Ind. Eng. Chem. Anal. Ed.*, 7, 165, 1935; B. Bullock and P. L. Kirk, *ib.*, 7, 178, 1935; E. Chirnoagă, *Zeit. anal. Chem.*, 101, 31, 1935; T. Akiyama and S. Yabe, *Journ. Pharm. Soc. Japan*, 55, 71, 1935; A. W. Wellings, *Adsorption Indicators*, British Drug Houses, Ltd., London.

[5] DICHLOROFLUORESCEIN SOLUTION.—Dissolve 0·1 grm. of dichlorofluorescein in 60 c.c. of alcohol, add 2·5 c.c. of 0·1N-sodium hydroxide solution, and dilute to 100 c.c. with water.— I. M. Kolthoff, W. M. Lauer and C. J. Sunde, *l.c.*

[6] T. Akiyama and S. Yabe (*l.c.*) find that, with fluorescein as indicator in the presence of alcohol, the titration can be carried out down to a chloride concentration of 0·00125N.

CHAPTER IV.

COLORIMETRY AND TURBIDIMETRY.

§ 36. Colorimetric Methods of Analysis—Colorimetry.

COLORIMETRIC methods for the determination of small quantities of a substance have attracted a great deal of attention, particularly in technical analyses.[1] They have been successfully used, *inter alia*, for the determination of iron, manganese, chromium, copper, lead, bismuth, titanium, sulphates, chlorides, ammonia, carbon, silica and phosphorus. They usually offer a quick, simple and elegant means of determining the amount of a given constituent, and they can sometimes be used in cases where the amount is too small for gravimetric or volumetric methods. Colorimetric processes are frequently, but not always, more rapid than gravimetric methods.

The choice between colorimetric, volumetric and gravimetric processes is determined by the particular problem in hand, but *gravimetric or volumetric methods should nearly always be used when large quantities of the given constituent are in question*—provided, of course, that reliable gravimetric or volumetric processes are available. For small quantities some colorimetric processes far surpass gravimetric processes in accuracy, while others are but crude approximations.

In colorimetry it is assumed that *if two solutions of the same colouring agent in the same solvent have the same tint, they will have the same concentration*, when the depths of the two liquids through which the light passes are the same. Hence, if the concentration of one of the solutions be known, the concentration of the other solution must be the same. This assumption may mean that if w_1 and w_2 respectively denote the weights of colouring matter in two solutions, and d_1 and d_2 the corresponding thicknesses of the solutions through which the light passes to the eye, then,

$$w_1/d_2 = w_2/d_1 \quad . \qquad . \qquad . \qquad . \qquad . \qquad (1)$$

Hence, if any three of these magnitudes be known, the fourth can be calculated by simple proportion. The comparison of the colours of the solutions is done in glass cylinders—called test glasses—made from clear, colourless glass. The instrument used for the comparison is called a *colorimeter*, or *tintometer*. There are three types of colorimeter used in this work.[2]

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[1] G. and H. Krüss, *Kolorimetrie und quantitative Spectralanalyse*, Hamburg, 1909. For discussions of colorimetry, see also N. School, *Chem. Weekb.*, **27**, 52, 1930; N. E. Pestov, *Zeit. anal. Chem.*, **89**, 9, 1932; F. L. Hahn, *ib.*, **90**, 330, 1932; H. Brückner, *ib.*, **99**, 419, 1934; N. A. Tananaev, *Zavodskaya Lab.*, **2**, 9, 1933; J. Guild, *Journ. Sci. Instruments*, **11**, 69, 1934; Istin, *14th Cong. Chim. ind.*, Paris, 1934; F. D. and C. T. Snell, *Colorimetric Methods of Analysis*, London, 1936.

[2] For an absolute colorimeter, see A. and W. Thiel, *Zeit. Elektrochem.*, **38**, 621, 1932; *Chem. Fabrik.*, 409, 1932; A. Thiel, *ib.*, 383, 1934; *Zeit. anal. Chem.*, **94**, 170, 1933.

§ 37. Duboscq's Dipping Colorimeter.

In this instrument[1] the depth of the liquid in each test glass through which the light passes can be varied until each liquid appears to have the same colour tint. The depth of the liquid in each tube is measured by a vernier and scale, and since the concentration w_2 of one solution is known, the concentration w_1 of the unknown solution follows at once from (1) above, where

$$w_1 = \frac{w_2 d_2}{d_1} \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (2)$$

Fig. 24 represents a photograph of the front of the apparatus. The operator stands on the right. Fig. 25 represents the path of the light inside the instru-

Fig. 24.—Duboscq's Colorimeter.
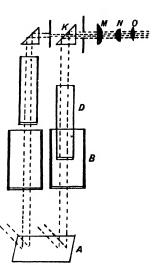
Fig. 25.—Course followed by Light in the Colorimeter.

ment. The diffused light of a lamp or of a monochromatic burner is the source of illumination. This light is reflected from the mirror A, and the right-hand beam passes through the fixed tube B and the movable tube D. This beam is reflected in the prism K and finally passes through the lenses MNO of the eyepiece. The optical arrangement is such that the beam illuminates an annular patch of the field. The left-hand beam follows a similar path and illuminates the centre of the annulus. Hence, the field is illuminated solely

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[1] H. Morton, *Chem. News*, **21**, 31, 1870. See also W. G. Smeaton, *Journ. Amer. Chem. Soc.*, **28**, 1433, 1906; O. Schreiner, *ib.*, **27**, 1192, 1905; G. Steiger, *ib.*, **30**, 215, 1908; C. H. Wolff, *Pharm. Ztg.*, **24**, 587, 1879; J. H. Long, *Journ. Amer. Chem. Soc.*, **38**, 716, 1916; J. C. Rook and S. R. Benedict, *Journ. Biol. Chem.*, **35**, 227, 1918; D. Wesson *et al.*, *Oil and Fat Ind.*, **5**, 173, 1928; F. Anselm, *Chem. Fabr.*, 504, 1929; E. Canals and E. Cabanes, *Bull. Soc. chim. biol.*, **14**, 238, 1932.

by the beams of light (dotted in the diagram) passing through the two sets of tubes.[1]

To illustrate by example: the solution of unknown concentration was made up to 250 c.c. and about 150 c.c. were placed in the left test glass of Duboscq's colorimeter. The standard solution containing 0·01 grm. of titanic oxide per 100 c.c., that is, 0·025 grm. per 250 c.c., was placed in the right test glass. The amount of liquid placed in the tubes must not be so great that liquid overflows when the tubes D are lowered to the bottom of B. Lower the tubes D until they touch the bottom of the tubes B. The verniers now mark zero, and the two halves of the field in the

FIG. 26.—Appearance in Eyepiece of Colorimeter.

eyepiece should be uniformly bright (fig. 26a); if not, the lamp illuminating the mirror A must be moved until the desired result is attained. Now raise the movable tube in the standard liquid until it reaches a point convenient for estimating the tint of the liquid. Then raise the other movable tube until equal tints are obtained in both fields (fig. 26c). Read the two scales. Suppose that for $w_2 = 0.025$, $d_2 = 2.1$ cm.; and $d_1 = 4.37$. Hence,

$$w_1 = 0.025 \times 2.10/4.37 = 0.0120 \text{ grm. per } 250 \text{ c.c.}$$

Fig. 26b represents the appearance of the field of view before the final adjustment (fig. 26c).

§ 38. Weller's Colorimeter.

Duboscq's colorimeter and similar instruments are expensive, and are only bought when it is probable that they will save in time what they cost in money. A cheaper instrument, quite efficient for most comparisons, can be made as described below. In this type of colorimeter the two test glasses are of the same width, and as the light passes horizontally through each $d_1 = d_2$. Consequently,

$$w_1 = w_2 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Hence, if w_2, in the case of titanic oxide, be 0·052 grm. per 250 c.c. of the standard solution, the same number will also represent the concentration w_1 of the titanic oxide in the unknown solution per 250 c.c., when the tints of the two solutions are the same. Weller's[2] and Hillebrand's colorimeters may be cited in illustration. These are easily made. A wooden box C, about 35 cm. long and 12 cm. square, is stained dead black[3] inside and out. The ends are open. A ground-glass partition is placed at B (fig. 27), and a blackened shutter S slides stiffly up and down 3 to 3·5 cm. behind the glass partition. Two test glasses are selected, of square section, 8 to 12 cm. high, and 3 to 3·5 cm. side. These glasses are placed between the two partitions when
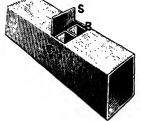
FIG. 27.—Weller's Colorimeter (modified).

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[1] To clean the apparatus, raise the tubes D, remove the tubes B, and take off the glass at the bottom. The tubes B and D can then be cleaned. Polish the rest of the apparatus with chamois leather.

[2] A Weller, *Ber.*, 15, 2599, 1882; W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, 700, 35, 1919; J. W. Mellor, *Trans. Cer. Soc.*, 8, 123, 1909.

[3] DEAD BLACK PAINT.—Dissolve shellac in methylated spirit; add French polish and then add lampblack. If the mixture dries a dead black which rubs off, more French polish or shellac is needed; if it dries light, more lampblack is needed.

in use.[1] Two methods of conducting the determination are indicated on pages 187 and 191.

J. W. Lovibond [2] has devised sets of "standard" coloured glasses; each set has the same colour, but the glasses are regularly graded in depth of tint. By superimposing glasses from the same and different sets—red, blue, yellow—composite colours can be obtained. In this way the tint of a liquid placed in a test glass with parallel sides at a definite distance apart can be matched, and the exact proportion of each component of the colour read off. By finding the tints of a series of standard solutions of known strength once for all, the standard tints so obtained render the subsequent preparation of a standard solution unnecessary provided the same method of preparation is employed. The instrument—"Lovibond's tintometer"—used for the comparison is similar in principle to the instrument indicated in fig. 27, but Lovibond has introduced several improvements which render the results much more accurate.

The tintometer has recently been adapted for the colorimetric determination of iron by the thiocyanate process [3] (page 185) and it is also used in the thioglycollic acid method (page 188).

§ 39. Nessler's Tubes.

A third method of comparing the tints is commonly used in water analysis. It is rather more tedious than the two methods which precede. The colour is developed in a solution of unknown strength and in a series of solutions of equal volume but of known strength. The two solutions of known strength which come nearest to the tint of the test solution are selected and the colour developed in another series of solutions within narrower limits. This method of trial and failure is repeated until the colour in the test cylinder matches the colour of the standard solution.

The comparison tubes should be selected with great care, and the bottoms should be regular. The bores of the test glasses should be uniform and not tapered.[4] As a matter of fact, the principle of the system is the same as that used in Weller's colorimeter. Although the cylinders are usually marked "25 c.c.," "50 c.c.," "100 c.c.," it is really the *lengths* of the columns, not the volumes of the solutions, which are compared. Hence, as in Weller's colorimeter, $w_1 = w_2$. It is obvious that in properly matched tubes the volume marks and the heights of the liquids should coincide.[5]

§ 40. Turbidity Methods of Analysis—Turbidimetry or Nephelometry.

Turbidity or nephelometric methods resemble colorimetric methods, but instead of comparing the different intensities of the colours of two solutions,

[1] Sold by dealers in chemical apparatus.
[2] J. W. Lovibond, *Journ. Soc. Chem. Ind.*, 7, 424, 1888; *Measurement of Light and Colour Sensations*, London; *An Introduction to the Study of Colour Phenomena*, London, 1905; O. Rosenheim and E. Schuster, *Biochem. Journ.*, 21, 1329, 1927; K. Sondén, *Arkiv. Kem. Min. Geol.*, 8, No. 7, 1, 1922; H. V. Arny and C. H. Ring, *Journ. Franklin Inst.*, 180, 199, 1915; K. S. Gibson, F. K. Harris and I. G. Priest, *U.S. Bur. Standards*, Sci. Paper No. 547, 1927; B. D. Judd, *ib.*, Research Paper No. 31, 1927.
[3] Private communication from the *British Refractories Research Association*, Stoke-on-Trent.
[4] See *British Stand. Inst.*, Specification 612, 1935.
[5] J. H. Yoe, *Ind. Eng. Chem.*, 19, 1131, 1927.

the degrees of opalescence of two solutions are compared.[1]   The opalescence is produced by the fine-grained solid matter in suspension, which settles very, very slowly and which is not usually removed by filtration in the ordinary manner.   For example, traces of silver chloride, barium sulphate and calcium oxalate.

The action of light on a turbid solution is twofold. (1) The light is dispersed. This gives the solution its characteristic colour. (2) The light is absorbed, so that an object viewed through the liquid appears with diminished distinctness. This latter is the quality compared.   It is well to prevent dispersion in the comparison of opalescent solutions as much as possible, by covering the cylinder with, say, a black cloth, and admitting the light from a circular aperture at the bottom.   The subject is discussed in more detail on pages 718 and 748.[2]

§ 41. Some Errors in Colorimetry and Turbidimetry.

The most important errors [3] in colorimetry arise from:

(1) *Imperfect perception of the colour.* Colour is a subjective phenomenon due to the action of light on the retina of the eye itself.   Possibly no two individuals see exactly the same colour tints in the same substance.   A person may be afflicted with a form of colour-blindness and be sensitive to one colour but not to another. Hence, the operator should test himself for any given colorimetric process by matching a standard colour of different intensities against itself.   If concordant results cannot be obtained, the operator must abandon that particular process.

It is here assumed that the operator is normally sensitive to colour impressions.   If a person of normal colour sensitiveness examines a coloured liquid with, say, the right eye over the cylinder, and then turns the head suddenly so that the left eye is over the cylinder, the colour *seems* less intense; in another moment, the right eye may be brought over the cylinder—again the colour seems less intense.   This shows that first impressions are the stronger, and that the impression imperceptibly weakens in intensity as the eye gets fatigued.   The eye quickly becomes fatigued and less sensitive to changes in the intensities of the tints.   The eye should therefore be frequently rested by looking on the floor, or into the dark corner of a room.[4]

There is also an appreciable difference in the sensitiveness of the two eyes for changes of colour.   Hence, many shield or close the less sensitive eye, and use the more sensitive eye for comparing tints.   The left eye, for example, is usually more sensitive than the right eye for variations in red tints, and hence the left eye is used for the colorimetric determination of iron.   A similar remark applies to the titanium yellow.   The eye requires more

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[1] T. W. Richards, *Proc. Amer. Acad.*, **30**, 385, 1894; T. W. Richards and R. C. Wells, *Amer. Chem. Journ.*, **31**, 235, 1904.

[2] For the calibration of nephelometers, see G. C. Whipple and D. D. Jackson, *Tech. Quart.*, **14**, 285, 1911; P. A. Kober and S. S. Graves, *Ind. Eng. Chem.*, **7**, 843, 1915; A. B. Lamb, P. W. Carleton and W. B. Meldrum, *Journ. Amer. Chem. Soc.*, **42**, 251, 1920; I. M. Kolthoff and H. Yutzy, *ib.*, **55**, 1915, 1933; J. H. Yoe, *Photometric Chemical Analysis*, New York, **2**, 137, 1929. For the adaptation of Duboscq's colorimeter for use as a nephelometer, see W. R. Bloor, *Journ. Biol. Chem.*, **22**, 145, 1915.

[3] W. M. Dehn, *Journ. Amer. Chem. Soc.*, **39**, 1392, 1917; F. F. Hahn and R. Klockmann, *Zeit. angew. Chem.*, **43**, 993, 1930; P. Fleury, *Bull. Soc. chim. biol.*, **4**, 223, 1922; Y. Garreau, *ib.*, **4**, 233, 1922; N. E. Pestov, *Zeit. anal. Chem.*, **89**, 9, 1932; R. A. Houston and A. J. Younger, *Phil. Mag.*, (7), **19**, 1107, 1935.

[4] N. E. Pestov, *Zeit. anal. Chem.*, **89**, 9, 1932; J. Guild, *Phil. Trans.*, **230 A**, 149, 1931.

experience in detecting differences of shade with yellow tints, *e.g.* in the titanium determination, than with many other colours.[1]

(2) *Unfavourable light.* The colours of the solutions might be compared with the light from a blue sky; light reflected from grey clouds, or clouds tinged with yellow or orange; light reflected from coloured objects; artificial light; or light which has been transmitted through a yellow fog. In each case, the effect of the incident light on the colour of the transparent solution is different. The source of the illumination is therefore of great importance in colorimetric work. In general, avoid artificial light and light tinged with yellow in, say, the titanium determination.

(3) *Differences in the concentration of the test and standard solutions.* The colour of many substances is quite different in concentrated and in dilute solution. The solvent absorbs a certain amount of light; consequently, the concentration of the standard and test solutions should be the same. In the determination of iron there is a reaction between the colouring agent— $Fe(CNS)_3$ —and the solvent, water, so that the amounts of iron with different amounts of solvent will not be represented by the relation (1) above. Hence Duboscq's type of colorimeter is not suitable for the colorimetric determination of iron.

(4) *Changes in the standard solutions.* The standard solutions may deteriorate in strength, and may also be contaminated with impurities derived from, say, the glass bottles in which the solutions are kept, or from the atmosphere of the laboratory when the solutions are temporarily exposed. Such impurities may be fatal to the accuracy of determinations of ammonia, nitrites and phosphates.[2]

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[1] Constant errors in the comparison of colours can be eliminated by the method of substitution in which a solution of *known* strength is substituted in the test glass, after the unknown solution has been compared with the standard.

[2] H. V. Arny and C. H. Ring. *Ind. Eng. Chem.*, 8, 309, 1916.

CHAPTER V.

FILTRATION AND WASHING.

A tremendous amount of time is consumed, often wasted, in the filtration and washing of precipitates for analytical work. Every device which will accelerate these fundamental operations, without interfering with their efficacy, must raise the efficiency of the laboratory.

§ 42. Filter-Paper.

THE purpose of filtration is to separate a solid from the liquid in which it is suspended. Filtration is usually effected by causing the liquid to pass through a medium which is porous enough to permit the passage of the liquid and compact enough to retain the solid. Among the different filtering media in use are cotton-wool, sand, charcoal, crushed and sintered glass, glass-wool, asbestos pulp, paper pulp, platinum felt, asbestos paper [1] and lastly, but most important of all, unsized paper—filter-paper.

Filter-paper should give no residue when distilled water or dilute hydrochloric acid is repeatedly passed through it and the liquid then evaporated to dryness; a 10 per cent. aqueous solution of salicylic acid should give no perceptible coloration (showing the absence of iron); ammonium sulphide should not blacken the paper; nor should a dilute soda solution, which has been repeatedly passed through the paper, give a turbidity when neutralised with an acid (showing the absence of oils and fats).[2] Analysts, however, are not much troubled about the quality of their filter-paper, because filter-papers of remarkably good quality—almost pure cellulose—can be easily obtained.

Filter-paper for analytical work should be kept in air-tight vessels. If the paper be exposed to laboratory fumes it may absorb acid, ammoniacal or other fumes, and disturb certain determinations,[3] e.g. determinations of the hardness of water. Paper which has been kept in an exposed place may subsequently liberate iodine from a solution of potassium iodide (free from iodate). Andrews, too, detected nitrites in filter-paper which had been kept some time in a laboratory.

After filtration and washing, the paper is usually heated in a weighed crucible together with the solid until only the ash of the paper remains, mixed with the calcined precipitate. The ash is weighed with the precipitate and an allowance is made for the additional weight due to the ash of the filter-paper. Owing to the fact that the precipitate has sometimes to be further investigated,

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[1] A. Convert, *Chem. Centr.*, (3), **16**, 850, 1885; A. Gruner, *Zeit. anal. Chem.*, **9**, 68, 1870; W. Johnstone, *Analyst*, **12**, 234, 1887.

[2] *Pharm. Post*, 252, 1896; L. Padé, *Bull. Soc. chim.*, (2), **47**, 243, 1887; W. Wicke, *Liebig's Ann.*, **112**, 127, 1859.

[3] H. R. Proctor, *Journ. Soc. Chem. Ind.*, **23**, 8, 1904; M. Mansier, *Journ. Pharm. Chim.*, (6), **16**, 60, 1902; E. Mallinckrodt and W. N. Stull, *Journ. Amer. Chem. Soc.*, **26**, 1031, 1904; L. L. de Koninck, *Bull. Soc. chim. Belg.*, **23**, 221, 1909.

it is an advantage to use filter-paper with as little ash as possible. By treating the best filter-paper with suitable acids, the manufacturer is able to reduce the amount of ash to a negligibly small quantity.[1] Indeed, the best filter-papers behave as if they were almost pure cellulose—*i.e.* almost ashless.

With such papers the amount of ash is so small that its weight can be neglected in routine work. If, however, the paper has been used in a filtration, the weight of the ash will not necessarily be the same as the weight of the ash of an unused paper.

The amount of ash given on burning a filter depends upon the nature of the liquid which has passed through the paper. A certain amount of fixed alkali, alkaline earth and some salts are retained by the cellulose of the paper very tenaciously. If a neutral solution be passed through the paper, the salts may be retained by the paper, as in the case of the fixed alkalies.[2] Acids remove traces of mineral substances from unwashed papers. Consequently the weight of the ash from an unwashed and unused paper may be greater than when the paper has been used for filtering acid solutions. In illustration, the following results (Table XIII.) were obtained for the ash of J. H. Munktell's No. 00 Swedish filter-papers which had been treated respectively with dilute sulphuric acid and potassium hydroxide, and subsequently washed until the wash-water gave no reaction with neutral litmus solution.

Table XIII.—Relation between the Filter-Paper Ash and Liquid Filtered.
(Grams of ash per paper.)

	5·5 cm.	7 cm.	9 cm.	11 cm.	12·5 cm.
Acid . . .	0·000011	0·000019	0·000031	0·000047	0·000061
Alkali . . .	0·000044	0·000071	0·000118	0·000176	0·000219

The inference is obvious. It is not sufficient to adopt the weight of the ash of the unused papers for a precipitate which has been isolated by the filtration of solutions containing salts which may be adsorbed by the filter-paper. In exact work, the amount of ash in papers which have been treated with solutions resembling those used in the given filtration must be determined for a given precipitate. However, the ash of these papers in neither case need be considered in most analyses.[3] Nowadays there is a large range of filter-papers available both for different purposes and for different types of precipitates.

To summarise, the desiderata in a filter-paper are: (1) porosity, to ensure rapid filtration; (2) sufficient compactness to ensure complete retention of the solid; (3) low amount of ash; and (4) freedom from impurities likely to contaminate deleteriously the material being filtered.[4] The first and second qualities are antagonistic. It is important to *adapt the size of the filter-paper to suit the precipitate to be washed. Use "rapid" (porous) papers for all pre-*

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[1] For slight acidity of acid-washed filter-paper, M. de la Source, *Ann. Chim. anal.*, **2**, 82, 1897.

[2] M. Mansier, *Journ. Pharm. Chim.*, (6), **16**, 60, 1902. See footnote 1, page 85.

[3] L. L. de Koninck (*Lehrbuch der qualitativen und quantitativen chemischen Analyse*, Berlin, **1**, 39, 1904) gives the following analysis, in round numbers, of the ash of Munktell's filter-papers: SiO_2, 32; Al_2O_3, 15; Fe_2O_3, 9; MnO, 8; MgO, 11; CaO, 21; CuO, trace; alkalies, 2; SO_3, 2; P_2O_5, 0·2; Cl, trace.

[4] R. S. McBride and J. A. Scherrer, *Journ. Amer. Chem. Soc.*, **39**, 928, 1917.

cipitates which do not readily pass through the paper and use the slow, compact papers only when absolutely necessary.[1]

§ 43. Filtration.

The *art* of quantitative analysis is largely dependent upon the skill exercised in transferring substances from one vessel to another without gain or loss.

Selecting the Funnel.—Do not use ribbed or guttered funnels for quantitative work. These often give trouble in washing. Finkener's funnel,[2] fig. 28, has a long capillary stem[3] and it is supposed
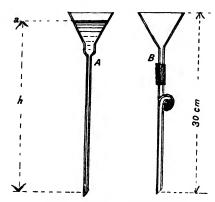
FIG. 28.—Long-stemmed Funnels.

to have smooth walls inclined at an angle of 60°, so that when the paper is folded—four-ply—and opened out in the regular manner, it will fit close to the walls of the funnel.[4] The folding of papers with creases[5] to expose a large surface and prevent the paper lying close to the wall of the funnel is not recommended,[6] because (1) precipitate and paper are more difficult to wash; (2) there is a greater risk of breaking the paper; and (3) filtration is not so rapid as when the stem of the funnel is kept filled with liquid.

Fitting the Filter-Paper in the Funnel. —When the paper is placed in the funnel it should not come nearer than half a centimetre to the top edge of the funnel and on no account should the paper project beyond the funnel. The diameters of funnels best suited for filter-papers of different sizes are indicated below:—

| Diam. of filter-paper | . | . | 5 | 7 | 9 | 11 | 12½ | 15 | 18 cm. |
| Diam. of funnel | . | . | 2½–3 | 4 | 5 | 6½ | 7½ | 9 | 10 cm. |

Place the paper in the *dry* funnel, wet the paper and carefully bed it against the walls of the funnel. When the paper is filled with water, the stem of the funnel should fill with a column of water[7] and air should not pass between

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[1] A. Gawalovski, *Zeit. anal. Chem.*, 16, 59, 1877; 18, 246, 1879; 37, 377, 1898; 54, 503, 1915; R. Fresenius and Caspari, *ib.*, 22, 241, 1883; K. Kraut, *ib.*, 18, 543, 1879; F. Mohr, *ib.*, 12, 148, 1873; A. von Wich, *Viertel. prakt. Pharm.*, 8, 187, 1859; J. J. Berzelius, *Lehrbuch der Chemie*, Dresden, 10, 260, 1835; H. Uelsmann, *Dingler's Journ.*, 220, 534, 1876.

[2] A. Gwiggnes, *Chem. Ztg.*, 27, 889, 1903.

[3] F. Weil, *Zeit. anal. Chem.*, 2, 359, 1863; I. B. Cook, *Chem. News*, 27, 261, 1873; 29, 81, 1874; J. F. Kerr, *ib.*, 29, 71, 1874; J. Piccard (*Zeit. anal. Chem.*, 4, 45, 1865; G. Lunge, *Chem. News*, 13, 23, 1866) proposed joining a narrow tube about 32 cm. long to an ordinary funnel by means of a piece of rubber tubing, as shown in fig. 28B. Piccard's knot, as the tube is called, is much used in qualitative analysis, but is less suited for quantitative work. We have given the different types of funnel on the market a three months' trial, and found those indicated in fig. 28A best for quantitative work.

[4] If the slope of the funnel be not quite right, it may be necessary to alter the crease of the filter-paper a little, so that the paper lies close to the walls of the funnel when opened out. If a very bad funnel is found in a batch, it may give more trouble than it is worth.

[5] C. E. Avery, *Chem. News*, 17, 294, 1868. See H. M. Schleicher (*Met. Chem. Eng.*, 16, 548, 1917) on folding filter-papers.

[6] P. Hart (*Chem. Ztg.*, 32, 1228, 1908) recommends folded papers for fine sand and colloidal precipitates.

[7] The filling of the stem of the funnel is facilitated by keeping the stem free from grease by frequent treatment with the cleaning mixture of page 29; and also by making two constrictions in the stem. P. E. Raaschou, *Zeit. anal. Chem.*, 49, 759, 1910.

the walls of the funnel and the paper as the paper empties. When the filter-paper is properly bedded, water will flow through the paper quickly [1] and filtration will usually proceed quite rapidly; at any rate, the paper is doing its best under the given conditions. The liquid in the filter-paper is under a pressure equal to the weight of a column of liquid of the same diameter as the bore of the stem and of a height h, fig. 28, where a represents the level of liquid in the filter-paper. Hence, in filtering, keep the paper filled to its greatest capacity [2] in order to get a maximum value for h, which, in turn, corresponds with maximum velocity of filtration. If the bore of the tube be too wide, liquid will run down the sides of the tube and no pressure will be produced; while if the tube be too narrow, surface tension may prevent the flow of the liquid even when the funnel is full. A sharp tap on the filter stand will often start the flow.[3]

In quantitative work it is very important to bear in mind that *the size of the filter-paper must be determined by the magnitude of the precipitate, not by the bulk of the liquid to be filtered.* If too large a paper be selected, time is wasted in washing the paper and it has just been pointed out that paper as well as precipitate has the property of retaining certain salts very tenaciously.

Transfer of Precipitate to Filter-Paper.—The precipitate is usually allowed to settle before filtration.[4] The clear liquid should not be poured directly into the funnel, but down a glass rod, so that the stream is directed towards the side, not the centre of the filter-paper.[5] The receiving vessel for the filtrate should be so placed that the liquid running from the funnel does not fall into the centre, but down the side of the vessel, thus avoiding any danger of loss by splashing. If desired, the receiving vessel for the filtrate can be covered by a glass plate with a hole at the side, whereby the position of the stem of the funnel is unaltered. The funnel can also be covered with a clock-glass while the filtration is in progress. The object is to keep out dust.

If it be noticed while a filtration is in progress that too small a paper has been selected, so that the precipitate is likely to fill the paper more than half full, it is better to use another paper and distribute the precipitate between the two papers. Ample room should be left for washing the precipitate. If the precipitate occupies more than two-thirds of the paper, difficulties will be encountered in the subsequent washing.

"Policeman."—When the liquid has been transferred to the paper, it will generally be found that small portions of the precipitate remain adhering to the vessel.[6] These can usually be loosened by means of a *"policeman,"* which is

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[1] If the water does not flow through sufficiently rapidly, discard the paper and use another.

[2] The capacity in c.c. of smooth filter-papers folded to fit a funnel with an angle of 60° is $\pi d^3 \sqrt{3}/192$, where d is diameter of the paper in cm.; if the paper is filled to within 0·5 cm. of the top edge, $(d-1)$ must be substituted for d.—L. Wolter, *Chem. Ztg.*, 38, 1243, 1914.

[3] Any dirt in the bore of these tubes is easily removed with a "tube cleaner" or a tobacco-pipe cleaner. E. Bauer (*Chem. Ztg.*, 12, 789, 1888) recommends a funnel with no stem at all for precipitates which filter with difficulty ! His idea is to let the funnel dip in a vessel of water. By renewing the water occasionally, the precipitate is washed by diffusion. There is no advantage in this suggestion for general work. See also P. Blackman, *Chem. News*, 104, 30, 211, 312, 1911.

[4] (1) Fine precipitates are then not so likely to run through the filter-paper; and (2) the time occupied in standing ensures more complete precipitation with precipitates which form slowly, *e.g.* magnesium ammonium phosphate, ammonium phosphomolybdate, potassium platinichloride, potassium cobaltinitrite.

[5] Do not stir up the liquid when the rod is returned to the liquid.

[6] If the particles cannot be scraped off, dissolve them in a suitable solvent and reprecipitate in a small beaker. In some cases, the particles need not be loosened, but left in the beaker. This is usually done when the precipitate is to be dissolved and reprecipitated, as is the case

made by covering the end of a glass rod with a tight-fitting piece of rubber tube. Pieces of rubber tube with solid ends are sold for the purpose, or they can be made from a piece of rubber tubing 3–4 cm. long by placing a little solution of caoutchouc in chloroform (or naphtha) within the rubber tubing at one end, and pressing the sides together between the jaws of a clamp [1] for a couple of days. The sealed end is then trimmed with a pair of scissors and the open end is slipped on to a piece of glass rod which fits the rubber tightly.[2] If an Erlenmeyer flask is used for the precipitation, care should be taken to choose one with a bottom easily accessible to the "policeman."

Washing the Precipitate.—After thoroughly washing the rod and "policeman," the adhering particles are loosened from the sides of the beaker by means of the "policeman." The beaker is then held between the thumb and the last three fingers of the left hand, while the rod, carrying the "policeman," is clamped across a diameter of the beaker by means of the forefinger. The beaker is now inverted over the filtering funnel until the rod is inclined at an angle of about 45° to the vertical. The nozzle of the wash-bottle having been turned upwards, the bottle is held in the right hand and small jets of the washing liquid are intermittently directed from it round and round the inside of the beaker. The liquid is allowed to drain completely from the beaker, down the rod and on to the side of the filter-paper, between each washing. In this way the walls of the beaker are effectively washed and all particles loosened by the "policeman" are transferred *via* the rod to the filter-paper. Finally the rod and "policeman" are well rinsed into the funnel. The washing of the precipitate on the paper is effected by means of a jet of, say, water from the wash-bottle. The stream is first directed round and round the upper edge of the filter-paper so as to wash downwards towards the apex of the cone and the precipitate is collected as nearly as possible at the apex of the cone at the last washing. *The paper is never filled with water and the precipitate is nearly always allowed to drain completely before adding fresh wash-water.* The washing is continued until a few drops of the washings collected in a test tube show the absence of the salts which are being washed from the precipitate.[3] Before testing, the end of the funnel should be rinsed as, owing to surface tension, the liquid tends to creep up the outside of the funnel. For a similar reason the top edge of the filter-paper needs thorough washing. The filtrate is usually needed for the determination of another constituent and, in consequence, as little of the washings as convenient must be used in making the test, otherwise some of the filtrate will be lost. Six washings may suffice, but there is no fixed rule. Some precipitates retain the mother liquid more tenaciously than others, partly attracted by some kind of surface action and partly entangled mechanically in the solid.

It may seem that undue stress is laid upon manipulation. The great accuracy and skill with which a competent analyst does his work can only be acquired by a repetition of the same operations a great number of times. There are some troublesome precipitates which at best require inconveniently large volumes of wash-water. When another constituent is to be separated

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with the "alumina" precipitate in clay analyses. The beaker and the particles are washed as well as possible, and the solution of the precipitate on the filter-paper is allowed to return into the beaker where the first precipitation was made.

[1] A clamp for the purpose is easily made from two pieces of wood, say, 30 cm. long, and 5 cm. by 2 cm. cross section. Holes are bored through each end to fit a pair of "sash screws." The rubber tips are clamped by turning the thumb-screws.

[2] A. A. Blair, *The Chemical Analysis of Iron*, Philadelphia, 31, 1908.

[3] In some cases, until a few drops evaporated on a piece of clean platinum foil give no residue.

from the filtrate, time is lost by the necessary evaporation and the risk of loss during transfer from vessel to vessel is increased. In such cases it is best to change the receiver as soon as the liquid is filtered and washing begins. Then collect the washings in an evaporating basin and concentrate them by evaporation to a convenient volume. Mix the concentrated washings with the first filtrate. It is a good plan to change the receiver regularly as soon as washing starts, so that if the filtrate begins to get turbid towards the end of a washing, there will be no need to refilter all the liquid. Experience will soon teach what filtrates and washings may be safely collected in one receiving vessel.

§ 44. Wash-Bottles.

A great many types of wash-bottle have been suggested. The simpler types generally are best. That shown in A and B, fig. 29, is the form most useful for general work. It is fitted with a rubber stopper [1] and glass tubes.
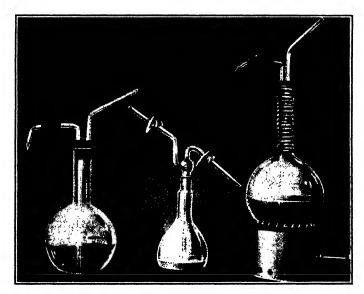
Fig. 29.—Wash-bottles.

The jet is joined by thick black rubber tubing so that it can easily be turned in any direction.[2] It is convenient to have several interchangeable jets with different sized orifices whereby the volume of the jet of liquid can be varied when desired. The neck of the flask is bound round with thick string, flannel, birch bark, cork or some suitable non-conductor of heat,[3] thus enabling the bottle to be used when necessary for hot wash liquors.

Some prefer Erlenmeyer or Sullivan flasks for wash-bottles. The wash-bottle, C, fig. 29, is used for alcohol or other volatile liquids or for liquids which

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[1] There is a danger of contaminating the water with sulphuric acid derived from the sulphides—antimony—used in vulcanising the rubber. J. Pattinson and J. T. Dunn, *Journ. Soc. Chem. Ind.*, 24, 16, 1905.

[2] G. Foord, *Chem. News*, 30, 191, 1874; A. R. Leeds, *ib.*, 20, 236, 1870; W. J. Land, *Amer. Chemist*, 3, 221, 1874; A. Gawalovski, *Zeit. anal. Chem.*, 14, 170, 1875.

[3] Asbestos paper is objectionable, because it is liable to flake off, and particles may thus get into the filter-paper or filtrate.

spoil in exposure to the air.[1]　It is fitted, as shown, with a ground glass stopper and has stop-cocks on the jet and mouth-piece.

When warming the contents of a wash-bottle it is customary to remove the stopper and ledge it on the neck of the bottle in order to prevent facial scalds by steam escaping from the mouth-piece.　If, however, the bottle is well shaken to expel any steam just before use, this precaution is unnecessary, though the rubber stopper deteriorates through continued exposure to steam. Alternatively a bottle fitted with a valve can be used.

Wash-bottles containing ammonia water, ammonium carbonate, hydrogen or ammonium sulphide solutions and other unpleasant liquids, are best fitted with some form of valve which is closed at will by the excess pressure in the flask.　Various types of valves have been devised,[2] most of which are illustrated in dealers' catalogues.

Washing a Large Number of Precipitates. — When a number of precipitates have to be washed, the wash-bottle can be almost discarded, and a water supply —"bottle and syphon"—placed high above the working bench.　The syphon tube is connected with a glass jet by a piece of rubber tubing sufficiently long to reach all the precipitates to be washed, and with a suitable tap for arresting or regulating the flow of the liquid used for washing the precipitates.　If water be the washing liquid, arrangements can easily be devised for heating the reservoir. This arrangement is much more convenient than wash-bottles.[3]

§ 45. The Theory of Washing Precipitates.

Under ideal conditions the reagent used for precipitations—the precipitant—should form a precipitate of definite composition, which is very sparingly soluble, or practically insoluble, in the mother and washing liquids.　Any excess of the precipitating agent should be readily removed from the precipitate by washing (or by ignition).　The precipitating agent should not introduce any substance likely to interfere with the precipitation of other constituents from the filtrate later on.　Again, the precipitate should be compact, easily filtered and washed.　Few processes satisfy all these desiderata, and an important part of analytical chemistry is to know what conditions favour and what conditions hinder the separation and purification of a given precipitate.　There are, however, a few general principles of such wide applicability that they should be carefully studied.

Colloidal and Fine-grained Precipitates.—In general, the finer the grain of the precipitate, the greater the quantity of contaminating salts retained by the wet precipitate.　Fine-grained precipitates expose a large surface of separation between the solid and solution.　The salts appear to be retained by a kind of

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[1] For compressed air wash-bottles, see W. C. Ferguson, *Journ. Amer. Chem. Soc.*, **16**, 149, 1894.

[2] For Bunsen's valve and some modifications, see page 170.　J. J. Griffin, *Brit. Pat. No.* 464801, 1905; M. Stuhl, *Chem. Ztg.*, **21**, 396, 1897; E. Stroschein, *ib.*, **13**, 464, 1889; C. E. Waters, *Journ. Amer. Chem. Soc.*, **27**, 298, 1905; R. K. Meade, *ib.*, **19**, 581, 1897; F. M. Haldeman, *Journ. Anal. App. Chem.*, **2**, 301, 1888; L. M. Dennis, *Amer. Chem. Journ.*, **11**, 218, 1889; E. Jacob, *Zeit. anal. Chem.*, **5**, 168, 1866; T. Bayley, *ib.*, **18**, 295, 1879; E. Borgmann, *ib.*, **22**, 60, 1883; H. Dubovitz, *Chem. News*, **91**, 147, 1905.

[3] G. E. Boltz, *Journ. Amer. Chem. Soc.*, **33**, 514, 1911.　For automatic filtration and washing, see E. Sinkinson, *Chem. News*, **106**, 49, 1912; *Analyst*, **45**, 94, 1920; E. C. Lanthrop, *Ind. Eng. Chem.*, **9**, 527, 1917; J. M. Pickel, *Chem. News*, **112**, 3, 1915; M. L. Hamlin, *Journ. Amer. Chem. Soc.*, **33**, 1584, 1911.　For filtering and washing in inert gases, see J. B. Firth and J. E. Myers, *Proc. Chem. Soc.*, **27**, 96, 1911; *Chem. News*, **103**, 223, 1911; G. Reddelien, *Chem. Ztg.*, **41**, 584, 1917; A. Wolfram, *Ber.*, **54B**, 857, 1921; V. Grabe and K. Freund, *Biochem. Zeit.*, **205**, 259, 1929.

surface attraction which is called, for convenience, adsorption.[1] Hence, fine-grained precipitates are more difficult to wash clean than coarse-grained precipitates.[2] Colloidal gelatinous precipitates like ferric and aluminium hydroxides are in an extremely fine state of subdivision, and, in consequence, they are most difficult to wash clean. Such precipitates may require ten to twenty washings, and then not be so clean as a coarse-grained crystalline precipitate after two or three washings.[3] The addition of a moderate amount of filter-paper pulp to the solution *after precipitation* often materially facilitates the filtration and washing of gelatinous precipitates by increasing their porosity.

Again, fine-grained precipitates, like newly precipitated barium sulphate, lead sulphite, calcium oxalate and silver chloride, are particularly liable to pass through the filter-paper, while coarse-grained precipitates give no trouble. Hence, the analyst uses various artifices in order to coagulate or to crystallise gelatinous and amorphous precipitates. Among the more important means of effecting these changes are: -

(1) The grain size can be frequently increased by allowing the precipitate to stand in the mother liquid for some time. This, for instance, is the case with lead chromate, antimony oxychloride, manganese ammonium phosphate, sodium antimonate, stannic hydroxide, calcium oxalate, silver chloride, metallic sulphides, barium sulphate, etc.[4]

(2) Precipitates produced in hot solutions are often coarser-grained than precipitates produced in cold solutions. The boiling of precipitates in a fine state of subdivision may lead to the flocculation of a large number of the fine particles into a relatively small number of coarse grains.[5] Zinc sulphide, barium sulphate and manganese ammonium phosphate may be cited in illustration.

(3) The flocculation of a precipitate which separates in a colloidal condition is frequently effected by the salts present in the mother liquid. When these salts have been almost removed, during the later stages of the washing, the coagulated precipitate sometimes passes to a colloidal or gelatinous condition, and it may then give a turbid filtrate, or become so slimy as to be almost impermeable to the washing liquid.[6] In such cases it is necessary to wash the precipitate, not with pure water, but with a solution of an acid or salt which will prevent the deflocculation of the precipitate and which can be easily removed by drying or ignition. Acids can only be used with precipitates of an acid nature, *e.g.* washing titanium hydroxide with acetic acid (page 195); and with precipitates insoluble in even strong acids, *e.g.* silver chloride, which is washed with dilute nitric acid (page 747). Usually, we have to depend upon the ammonium salts --nitrate, sulphate, chloride and acetate.[7] For instance,

[1] For adsorption in analytical work, see I. M. Kolthoff, *Pharm. Weekb.*, 57, 1510, 1571, 1920; 58, 46, 152, 401, 463, 1921.

[2] The term "coarse-grained precipitate" of course does not mean aggregates formed by the clotting of a number of fine grains.

[3] P. Nicolardot, *Compt. rend.*, 140, 310, 1905; J. Duclaux, *ib.*, 143, 296, 1906; G. N. Wyrouboff, *Ann. Chim. Phys.*, (8), 7, 449, 1905.

[4] G. Watson, *Chem. News*, 63, 109, 1891.

[5] A. Villiers, *Compt. rend.*, 120, 97, 149, 1895.

[6] For the clogging of filters, see G. Génin, *Rev. gén. Colloid*, 5, 523, 1927.

[7] R. Bunsen, *Liebig's Ann.*, 106, 13, 1858. Salts of polyvalent metals and alkaline earths give the best results, but these, with the exception of mercury, are excluded because they would remain with the precipitate after ignition. Mercury salts can only be used in a limited number of cases on account of secondary reactions. Ammonium salts are perhaps least effective, but they are usually the best we can use. See R. G. Smith, *Journ. Soc. Chem. Ind.*, 16, 872, 1897; N. Pappada, *Zeit. Chem. Ind. Kolloide*, 9, 233, 1911; A. Villiers, *Compt. rend.*, 120, 188, 1895.

washing the "alumina" precipitate with ammonium nitrate (page 165).   The ammonium salt is volatilised when the precipitate is calcined.[1]

Adsorption of Salts by Precipitates.—On account of the adsorption of a certain amount of salt with colloidal precipitates, such as occurs, for instance, in the ammonia precipitate, the contaminating salts cannot be all removed by washing.   There are many reasons for supposing that all precipitates carry down with them, that is, adsorb, substances from the solution in which they are formed.   The wash-water may show no indication of the impurities so retained by the precipitate.   Thus, Warington [2] found that ferric hydroxide precipitated by potassium carbonate only lost two-thirds of this salt by a washing which would have removed all but a 0·0069th part of a salt not adsorbed by the precipitate.   The same observer records the adsorption of various salts by aluminium and ferric hydroxides.   It is therefore frequently advisable to dissolve the precipitate in a suitable solvent and reprecipitate. The objectionable impurity divides itself in a definite ratio between the precipitate and mother liquid.   A relatively large amount may be retained by the precipitate during the first precipitation, but on a second precipitation, when only that amount of salt which was retained by the first precipitate is in solution, the partition of the undesirable salt between the precipitate and the solution in the given ratio means that a relatively small amount of impurity will be retained by the second precipitate.   Two, possibly three, precipitations will generally remove all appreciable amounts of the objectionable impurity from the precipitate.   For instance, aluminium and ferric hydroxides, manganese ammonium phosphate (page 397), zinc sulphide (page 385) and nickel and cobalt sulphides (page 413).   Suppose that the first precipitate retains a 0·01th part of the objectionable salts, while a 0·99th part is removed by filtration.   The second precipitate will contain 0·01th of 0·01th of the salt; the third precipitate, 0·000001th of the salt.   Thus, repeated reprecipitation will soon carry the amount of impurity outside the range of the balance.[3]

These facts also lead us to conclude that, if a small quantity of a substance A is to be separated from a large quantity of a substance B, it is generally better to precipitate A rather than precipitate B.   The loss of A through adsorption by B makes the "error of experiment" greater than if some of B be lost through adsorption by A.

Amount of Liquid Needed for Washing Precipitates.—A rather important question has to be decided in washing precipitates.   Is a relatively small number of washings with large volumes of liquid more effective than a relatively large number of washings with small volumes of liquid?   Suppose that a precipitate be allowed to drain on a filter-paper, and that the precipitate exercises no physical or chemical action on the salts in solution in the mother liquid.[4]   Let the volume of the mother liquid retained by the moist precipitate

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[1] See page 384.   Sometimes precipitates which are difficult to filter clear can be satisfactorily filtered if a little recently ignited kieselguhr (J. P. Ogilvie, *Journ. Soc. Chem. Ind.*, **30**, 62, 1911), or china clay (F. Watts and H. A. Tempany, *ib.*, **27**, 53, 1908), be added to the mixture—*e.g.* for lead sulphite.   The device is particularly useful when the filtrate is alone wanted, or when the precipitate is to be afterwards dissolved in a solvent which does not attack the clay or silica.

[2] R. Warington, *Journ. Chem. Soc.*, **21**, 1, 1868; P. Jannasch and T. W. Richards, *Journ. prakt. Chem.*, (2), **39**, 321, 1889; Ed. Schneider, *Zeit. anal. Chem.*, **10**, 425, 1882; T. W. Richards, *ib.*, **46**, 189, 1903; *Proc. Amer. Acad.*, **35**, 377, 1900; K. Scheringa, *Pharm. Weekblad*, **48**, 674, 1911.

[3] In the case of some "rare earth" separations, where the ratio is relatively large, a great number of precipitations—fractional precipitations—may be required to effect the separation. W. Crookes, *Chem. News*, **54**, 131, 1886; K. Scheringa, *Pharm. Weekblad*, **48**, 674, 1911; G. McP. Smith, *Journ. Amer. Chem. Soc.*, **39**, 1152, 1917.

[4] The assumption is rarely justified, but this does not affect the principle under discussion.

be represented by v c.c. Add V c.c. of water to wash the precipitate. The total volume of liquid will be $(v + V)$ c.c. Let this drain on the filter-paper. The moist precipitate retains v c.c. of the $v + V$ c.c. Otherwise expressed, the precipitate on the first draining retains $\dfrac{v}{V+v}$ c.c. of the mother liquid. After the first washing, again add V c.c. of water and let the precipitate drain. The moist precipitate retains, on the second draining, a volume $\dfrac{v}{V+v}$ of the $\dfrac{v}{V+v}$ c.c. of the mother liquid. Hence, the precipitate retains:

First draining $\left(\dfrac{v}{V+v}\right)$ c.c. of the mother liquid;

Second draining $\left(\dfrac{v}{V+v}\right)^2$ c.c. of the mother liquid;

nth draining $\left(\dfrac{v}{V+v}\right)^n$ c.c. of the mother liquid.

In order to understand what these expressions symbolise, it is advisable to take a numerical example. Suppose that a precipitate, which retains at each draining $v = 1$ c.c. of the mother liquid, is to be washed until it retains but $0 \cdot 00001$ c.c. of the mother liquid. In that case, after the nth washing, we have

$$\left(\frac{1}{1+V}\right)^n = 0\cdot00001$$

If $n = 6$, V is nearly 6 c.c., and if $n = 4$, V is nearly 17 c.c. This means that the precipitate will be washed as clean with six washings ($n = 6$), using 6 c.c. of water ($V = 6$) each time, as with four washings ($n = 4$), using 17 c.c. ($V = 17$) each time. In the former case, 36 c.c. of wash-water pass through the filter-paper, and in the latter case, 68 c.c. of water pass through the filter-paper. Hence it may be concluded that *the washing of a precipitate is more efficiently performed by the frequent application of a small volume of water than by using a relatively large volume of water applied a small number of times.* It is here assumed that the precipitate is allowed to drain before it is refilled with washing liquid.[1] This theory of washing precipitates was developed by Bunsen, in 1868.[2]

Horsley deduces from his experiments:

1. To keep down the volume of the wash-water, keep the quantity of liquid on the filter-paper small throughout.

2. The time required for washing cannot be quickened or delayed by any change in the method of adding the wash liquid, provided the upper edge of the filter-paper be attended to.

3. To minimise the drudgery of filtration, make each addition as large as possible and allow the precipitate to drain; but the time of washing will not be affected.

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[1] In washing by decantation with boiling water, T. W. Das (*Chem. News*, 101, 169, 1910) recommends transferring the precipitate, after each decantation, to the filter, washing out the precipitate into a beaker, adding fresh water and repeating. This ensures the better removal of the mother liquid and more rapid washing.

[2] R. Bunsen, *Liebig's Ann.*, 148, 269, 1868; G. F. Horsley, *Chem. News*, 87, 237, 1903. For the theory of filtration, see A. J. V. Underwood, *World Eng. Cong. Tokio*, Paper No. 278, 1929; J. P. M. van Gilse, P. J. H. van Ginneken and H. I. Waterman, *Journ. Soc. Chem. Ind.*, 49, 444T, 483T, 1930; 50, 41T, 95T, 1931; B. F. Ruth, R. E. Montonna and G. H. Montillon, *Ind. Eng. Chem.*, 23, 850, 1931; C. Almy, junr., and W. K. Lewis, *ib.*, 4, 528, 1912.

§ 46. Bunsen's System of Accelerated Filtration.

The long-stemmed funnels we have just recommended give very good results in routine work, but a considerable amount of time can be saved by using suction, as recommended by Bunsen.[1]   The Swedish filter-papers mentioned on p. 79 will not bear much suction.   They will burst near the tip.   In consequence, a small perforated platinum filter cone, fig. 30, is placed in the funnel to help the paper to bear the pressure.[2]   The filter cone is first placed in the funnel, and the paper is bedded to cone and funnel.   If the paper be not properly bedded to both cone and funnel, it will inevitably be torn as soon as strong suction sets in.   The funnel is fixed in the neck of a stout-walled filtration flask by means of a rubber stopper.   If the filtrate is to be used afterwards, Witt's filtration jar may be preferable.[3]   Zöpfchen's[4] filtration tube is useful when small quantities are under investigation and in other special cases.   Instead of a platinum cone, filter-papers with toughened tips are useful when the pressure is not too great.[5]   These are made by immersing the tip of the folded paper in nitric acid (sp. gr. 1·42) for a few moments and then thoroughly washing the paper with water, or they can be purchased.   The small sizes (4 or 5·5 cm.) can be used in place of the platinum cone.   The toughened paper cone can be pierced in a number of places near the tip with a fine needle.[6]

Fig. 30.—Filter Cone.

In filtering and washing precipitates under diminished pressure, as a rule do not allow the precipitate to drain, but add more liquid before the former liquid has run through.   If the precipitate be allowed to drain, as recommended for ordinary filtration, channels or fissures sometimes form in the precipitate.   The wash-water then simply runs through the channels without coming in contact with the bulk of the precipitate.

§ 47. Tared Filter-Papers.

Some precipitates, when collected on a filter-paper, cannot be ignited with the paper on account of volatilisation or decomposition.   These cases require special treatment.   In some cases the filter-paper is separated from the precipitate and ignited separately.   In other cases the filter-paper is dried at, say, 100° or 120° and weighed.[7]   The precipitate is then collected and

[1] R. Bunsen, *Liebig's Ann.*, 148, 269, 1868; *Zeit. anal. Chem.*, 8, 174, 1869; E. C. Hildebrand, *Chem. News*, 34, 57, 1876; C. Jones, *Journ. Anal. App. Chem.*, 1, 383, 1887; V. Kreusler, *Chem. Ztg.*, 8, 1324, 1885.   For filtration under pressure, T. Feller, *Zeit. anal. Chem.*, 3, 325, 1864.

[2] A. Gawalovski, *Zeit. anal. Chem.*, 23, 372, 1884.   R. S. Dale, *Chem. News*, 20, 128, 1869, for copper cone.   See, and for funnels with a perforated inner wall, C. Nickles, *Journ. Soc. Chem. Ind.*, 6, 134, 1887; J. de Mollins, *Zeit. anal. Chem.*, 19, 334, 1880.

[3] O. N. Witt, *Chem. Ind.*, 510, 1899; A. R. Leeds, *Chem. News*, 23, 177, 1871; 21, 236, 1870; A. Burgemeister, *Zeit. anal. Chem.*, 28, 676, 1889; F. Allihn, *ib.*, 26, 721, 1887.

[4] H. Zöpfchen, *Chem. Ztg.*, 25, 1008, 1901; H. S. Bailey, *Journ. Amer. Chem. Soc.*, 31, 1144, 1909; W. M. Thornton, junr., *Ind. Eng. Chem.*, 10, 132, 1918.

[5] E. E. Francis, *Journ. Chem. Soc.*, 47, 183, 1885; J. F. Stoffart, *Journ. Anal. App. Chem.*, 4, 1, 1890; C. R. C. Tichborne, *Pharm. Journ.*, (3), 2, 881, 1871.   For the use of membrane filters, see R. Zsigmondy and W. Bachmann, *Zeit. anorg. Chem.*, 103, 119, 1918; R. Zsigmondy and G. Jander, *Zeit. anal. Chem.*, 58, 241, 1919; G. Jander and H. C. Stuhlmann, *ib.*, 60, 289, 1921; G. Jander, *ib.*, 61, 145, 1922; G. and W. Jander, *ib.*, 63, 273, 1923; L. Moser and T. Kittl, *Chem. Ztg.*, 44, 637, 1920.

[6] M. H. Cochrane, *Chem. News*, 32, 80, 1875.

[7] C. Gilbert, *Rep. Anal. Chem.*, 1, 264, 1881; J. L. Smith, *Chem. News*, 31, 55, 1875.

washed on the filter-paper as usual. The paper and contents are then partially dried in the funnel (so that the paper and contents can be removed without tearing the paper), placed in the weighing bottle and later dried at the desired temperature, say, 110° or 120°. The paper is very hygroscopic, and it must be protected from the atmosphere while being weighed. Consequently, the paper may be folded and placed between a pair of weighed watch-glasses, *e*, fig. 1 , or in weighing tubes, *f*, fig. 1. Some papers, after use, are liable to disintegrate and break if folded; in that case, either a Reinhardt weighing bottle, fig. 31, or a Koninck weighing funnel should be used.[1]

Fig. 31.—Reinhardt's Weighing Bottle.

If an allowance has to be made for the action of the liquid under filtration on the paper, it will be necessary to treat a second paper with the clear filtrate and find the effect on the weight of the paper after the paper has been washed and dried.[2] The loss or gain in the weight of the empty paper, by the treatment, represents the effect of the solution on the filter-paper containing the precipitate, and an allowance must be made accordingly.[3] The following is the best plan:—Two filter-papers of the same size are weighed one against the other. The difference in weight is marked with a pencil on the heavier. Each filter-paper is placed on a funnel. The solution to be filtered is poured through the one, and the filtrate is poured through the second paper. Similarly, duplicate the washings. The two filter-papers are dried in the ordinary manner. In weighing, the empty paper is placed on the right pan as a tare to the other, and due allowance made for the excess in the weight of the one paper over the other.[4]

A certain amount of judgment is required in using the different weighing tubes. For example, the Koninck's apparatus weighs about 50 grms. The precipitate may weigh 0·005 grm. The apparatus is thus 10,000 times heavier than the precipitate! The large surface exposed by the glass may introduce a small error which is relatively large in comparison with the substance being weighed. In general, the greater the difference between the weight of the precipitate and the weight of the apparatus, the greater the percentage error affecting the determination. It is therefore best to keep the weighing apparatus as small as possible. Processes involving the use of tared filter-papers are rapidly falling out of use.

§ 48. Filtration Tubes.

Instead of using tared filter-papers, substances which are injured by burning filter-papers may be filtered through cotton-wool,[5] asbestos,[6] felt cloth [7] or glass-wool.[8] Thus, a tube shaped as indicated in fig. 32 A—F. Allihn's

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[1] C. Reinhardt, *Zeit. angew. Chem.*, **2**, 61, 1889; L. L. de Koninck, *ib.*; **1**, 689, 1888.

[2] For the adsorption of salts by filter-paper, see footnote 1, page 85.

[3] If any solid matter should escape the first paper and be retained by the second, the work would probably be stultified. This is the objection to placing the second paper below the first in the funnel while the liquid is being filtered, and separating the papers later on for weighing.

[4] C. Rüdorff, *Zeit. angew. Chem.*, **3**, 633, 1890; *Chem. News*, **66**, 25, 1892.

[5] A. B. Clemence, *Journ. Anal. App. Chem.*, **1**, 273, 1887.

[6] See Gooch crucibles, page 91; W. P. Barba, *Chem. News*, **65**, 101, 1892.

[7] R. Frühling and J. Schuz, *Zeit. anal. Chem.*, **13**, 146, 1874.

[8] It is well to remember that the glass-wool is often made from lead glass, and may give up some lead to acid solutions. F. Muck, *Zeit. anal. Chem.*, **19**, 140, 1880; L. Blum, *ib.*, **31**, 292, 1892; F. Stolba, *ib.*, **17**, 79, 1878; R. Böttger, *Notizblatt*, **34**, 3191, 1884; M. Battandier, *Journ. Pharm. Chim.*, (4), **30**, 55, 1879; J. M. Wilkie and H. S. Anderson, *Journ. Soc. Chem. Ind.*, **36**, 272, 1917; W. M. Thornton, junr., *Ind. Eng. Chem.*, **10**, 132, 1918. For paper pulp, see S. L. Jodidi and E. H. Kellogg, *Journ. Franklin Inst.*, **181**, 217, 1916; O. Hackl, *Chem. Ztg.*, **43**, 70, 1919.

tube—may be packed first with glass-wool, then with, say, asbestos. Some precipitates are liable to clog if the asbestos be packed in too thick a layer —for instance, manganese oxide precipitated by potassium chlorate. In that case, some prefer a small plug of glass-wool, followed by a 0·6 to 0·7 cm. layer of calcined Calais sand,[1] with or without a thin layer of asbestos over the
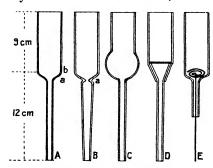
FIG. 32.—Filtration Tubes.

sand. Several different ways of packing have been suggested and several different forms of filter tube,[2] e.g. the tube may be stoppered at each end—Jannasch's filter tube, fig. 159, page 747. In Fresenius' filter tube there is a constriction a, fig. 32 B; and the tube may have a bulb in the region of the packing, fig. 32 C, which is Gibbs and Taylor's tube. In Mason's filter tube, D, fig. 32, the stem is separate from the body of the tube, so that, when in position, it forms a ledge on which a perforated "filter plate" can rest. The stem is rather longer than the body of the tube, so that it can be used to eject the filter bed.

In the analysis of iron where the carbon is separated as insoluble matter, the carbon is filtered in a tube of various forms— e.g. a platinum tube with a perforated removable disc which is covered with asbestos before filtration; a glass tube with a platinum spiral,[3] fig. 32 E, covered with long fibre and ignited asbestos. The carbonaceous matter is afterwards dried and burnt in a current of oxygen, or treated by the wet combustion process. Several other modifications are in use.[4] Thus, the carbon may be collected directly in a platinum boat fitted with a suitable bottom and holder for the filtration flask.

§ 49. Filtration through Perforated Discs and Funnels.

In 1870, Carmichael[5] proposed a different system of filtration from those which precede. Carmichael's plan was to keep the solution in a platinum dish in which the precipitate was to be finally weighed. A disc of filter-paper was placed against the lower perforated surface of the vessel, whose interior was connected with the suction apparatus. The liquid and wash-water was sucked from the vessel and the precipitate was prevented from leaving the vessel by the filter-

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[1] C. M. Sargent and J. K. Faust, Journ. Amer. Chem. Soc., 21, 287, 1899; Chem. News, 79, 158, 1899. S. Kern, ib., 38, 157, 1878, platinum tubes with asbestos packing. P. Weisskopf, Dingler's Journ., 206, 243, 1872, felted glass-wool packing.

[2] R. Fresenius, Zeit. anal. Chem., 8, 154, 1869; O. Lohse and P. Thomaschewski, ib., 39, 158, 1900; W. Gibbs and E. R. Taylor, Amer. J. Science, (2), 44, 215, 1867; F. Allihn, Journ. prakt. Chem., (2), 22, 56, 1880; F. Soxhlet, ib., (2), 21, 231, 1880; A. Goske, Chem. Ztg., 22, 21, 1898; Ber., 32, 2142, 1899; J. S. C. Gray, Chem. News, 72, 165, 1895; H. P. Mason, ib., 91, 180, 1905; T. Macfarlane, Analyst, 18, 73, 1895.

[3] T. M. Drown, Tech. Quart., 20, 552, 1891.

[4] E. Trutzer, Chem. Ztg., 38, 55, 1914; R. Peters, Zeit. angew. Chem., 27, 64, 1914; H. Häusler, Zeit. anal. Chem., 64, 361, 1924; A. Benedetti-Pichler, ib., 64, 409, 1924; P. W. Shimer, Journ. Amer. Chem. Soc., 27, 287, 1905; E. C. Bingham, Ind. Eng. Chem., 17, 293, 1925.

[5] H. Carmichael, Zeit. Chem., (2), 6, 481, 1870; Chem. News, 24, 213, 1871; W. Jago, ib., 33, 54, 1876; C. Ville, ib., 30, 200, 1874; J. P. Cooke, Proc. Amer. Acad., 12, 125, 1877; W. A. Puckner, Journ. Amer. Chem. Soc., 15, 710, 1893; R. Frühling and J. Schulz, Zeit. anal. Chem., 13, 146, 1874; L. W. Bahney, Met. Chem. Eng., 10, 737, 1912.

paper. Casamajor[1] modified this by using a kind of perforated false bottom with an aspirator and covering the upper surface of the perforated plate with a disc of filter-paper or asbestos pulp. Any liquid poured into the dish could then be filtered by suction through the perforated bottom. Sauer[2] suggested the use of flat discs of platinum gauze; and Grosjean perforated platinum discs in an ordinary funnel. A piece of filter-paper, rather larger than the disc, was supposed to be placed on the upper surface of the perforated disc. The paper was wetted and pressed close against the disc and funnel, so as to form a watertight joint all round the disc. The chief objection to the use of these discs for quantitative work arises from the fact that only part of the precipitate collects on the disc; part collects on the funnel, whence it can only be removed with difficulty. In order to keep the discs horizontal, Smith[3] soldered a platinum rod to the under side of the disc. When the rod was dropped into the stem of the funnel, the disc was in a horizontal position. The so-called Witt's filter plates[4] are made of glass or porcelain, rather larger in diameter on the upper side; otherwise they resemble Grosjean's discs, and Kaehler added the

Fig. 33.—Hirsch's Funnel.

vertical rod as previously suggested by Smith. Kaehler's filtration discs are also made with a groove to take a rubber band between the disc and the funnel, thus ensuring a better joint between plate and funnel. They are sometimes made of porous earthenware, asbestos or alundum (fused alumina) without perforations and of different porosities.[5] In Hirsch's[6] funnels (fig. 33) the disc is an integral part of the funnel. In the different forms of the so-called Büchner funnels the disc may or may not be permanently fixed, but the walls of the funnel above the disc are vertical. The sloping sides of the funnel below the disc narrow rapidly. The disc presents a more extended surface than in Hirsch's funnel. These are all different modifications of the one principle. Some of these funnels are valuable auxiliaries in preparation work. They are used with perforated rubber stoppers, filtering flask and suction. For other forms see page 716.

§ 50. Gooch Filtration Crucibles.

In 1878, F. A. Gooch[7] proposed to filter certain liquids by suction through a bed of asbestos resting on the perforated bottom of a crucible, the **Gooch crucible**. This type of crucible is so widely known and so much used in

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[1] P. Casamajor, *Amer. Chem.*, **5**, 440, 1875; **6**, 124, 1876; *Chem. News*, **32**, 33, 45, 183, 1875; **45**, 148, 1882; **46**, 8, 1882; **53**, 194, 248, 1886; *Journ. Amer. Chem. Soc.*, **3**, 125, 1881; **8**, 17, 1886; K. Zulkowsky, *Zeit. anal. Chem.*, **17**, 198, 1878; **18**, 459, 1879; **22**, 173, 1883. For reversed filtration, see also A. Wildenstein, *ib.*, **1**, 432, 1862; M. C. Lea, *Amer. J. Science*, (2), **42**, 379, 1866; E. Fleischer, *Chem. News*, **19**, 169, 1869.

[2] A. Sauer, *Zeit. anal. Chem.*, **14**, 312, 1875; B. J. Grosjean, *Journ. Chem. Soc.*, **16**, 341, 1879; *Chem. News*, **39**, 182, 1879; **45**, 107, 1882.

[3] J. C. Smith, *Amer. Chem. Journ.*, **1**, 368, 1879; S. L. Penfield and W. M. Bradley, *Amer. J. Science*, (4), **21**, 453, 1906; *Chem. News*, **94**, 293, 1906.

[4] O. N. Witt, *Ber.*, **19**, 918, 1886; M. Kaehler, *Zeit. anal. Chem.*, **33**, 63, 1894; *Journ. Amer. Chem. Soc.*, **16**, 58, 1894; C. H. Piesse, *Chem. News*, **28**, 198, 1873; A. Bornträger, *Ber.*, **19**, 1690, 1886. R. Warington (*Zeit. anal. Chem.*, **25**, 354, 1886) used lead plates for tartaric acid.

[5] R. C. Benner and W. H. Ross, *Journ. Amer. Chem. Soc.*, **34**, 51, 1912.

[6] R. Hirsch, *Chem. Ztg.*, **12**, 340, 1888; E. Büchner, *ib.*, **12**, 1277, 1888; **13**, 95, 1889; E. Murmann, *Zeit. anal. Chem.*, **50**, 742, 1911.

[7] F. A. Gooch, *Proc. Amer. Acad.*, **13**, 342, 1878; *ib.*, **20**, 390, 1885; *Chem. News*, **37**, 181, 1878; *ib.*, **53**, 234, 1886; G. C. Caldwell, *Journ. Amer. Chem. Soc.*, **13**, 105, 1891; T. Paul, *Zeit. anal. Chem.*, **31**, 537, 1892; *Chem. News*, **67**, 8, 1893.

analytical work that its preparation and use need no detailed description. Certain points, however, need amplification.

1. *Preparation of the Asbestos.*[1]—There are several varieties of asbestos on the market. The long-fibre "silky" crysolite asbestos gives the best results, since it does not pack so closely as many of the other varieties and, in consequence, it filters most rapidly. Place a 10's brass wire sieve, bottom upwards, on a sheet of paper. Rub a handful of asbestos roughly over the sieve so as to break the asbestos into smaller fragments which pass through the sieve.[2] Collect that which remains on the sieve into another bundle and repeat the operation until sufficient fibre has passed through. Next remove the dust and the fine powder by placing the material on a 30's lawn and agitating the mass while water is poured over the sieve. When the water which passes through has lost its milky appearance and seems quite clear, transfer the washed asbestos to a beaker or flask and boil for about half an hour with hydrochloric acid (1 : 4). Now wash the asbestos on a perforated funnel Hirsch's or Büchner's—fitted with a piece of filter-paper. Mix the washed asbestos with water, and the asbestos emulsion so prepared may be kept in a bottle ready for use. Asbestos already prepared for use in Gooch crucibles can be purchased.

2. *Sources of Error.*—Asbestos dried at 100° 110° to a constant weight may lose between 0·001 and 0·002 grm. of moisture on ignition. It is therefore necessary to dry or ignite the packed crucible for the same length of time and at the same temperature as that intended for the precipitate.[3] It is important, also, to remember that calcined asbestos may adsorb appreciable amounts of alkali not removed by washing. Most of the asbestos of commerce is also slightly attacked by water and feebly acid solutions.[4]

If the precipitate is to be ignited, the Gooch must be placed within a larger crucible or in a Gooch saucer and heated, at first gently, and then at the desired temperature.

The same crucible can be used for a number of determinations of the same substance. When the collection of precipitates in the crucible becomes too large, the upper part can be removed or the crucible recharged.

The Gooch crucible has deservedly won a permanent place in general analytical practice. It is exceptionally valuable when precipitates are to be redissolved from the felt after washing (*e.g.* sodium titanate in hydrochloric acid); when a mixed precipitate is to be separated into parts by appropriate solvents (*e.g.* washing antimony sulphide free from sulphur by carbon disulphide); separation of sulphides, soluble and insoluble in alkali sulphides, and generally when the desired solvent attacks filter-paper and not asbestos.

A filter tube is usually preferable to the Gooch crucible when it is necessary to heat the precipitate in a current of gas.[5]

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[1] P. Casamajor, *Chem. News,* **47,** 17, 1883; T. Paul, *Zeit. anal. Chem.,* **31,** 543, 1902; W. P. Barba, *Journ. Anal. App. Chem.,* **5,** 596, 1891; **6,** 35, 1892; *Chem. News,* **65,** 101, 1892; P. A. Kober, *Amer. Chem. Journ.,* **41,** 430, 1909; S. Matsuoka, *Journ. Chem. Soc. Japan,* **52,** 560, 1931; E. Cattelain, *Bull. Soc. chim.,* (4), **47,** 1404, 1930.

[2] Or scrape the fibrous asbestos down with a knife.

[3] Or find the amount of moisture retained by the dry Gooch crucible and make the necessary allowance when the precipitate is weighed. G. Auchy, *Journ. Amer. Chem. Soc.,* **22,** 46, 1900; H. Theile, *Zeit. öffent. Chem.,* **7,** 388, 1901; K. Windisch, *Chem. Centr.,* **75,** ii, 1621, 1905; M. Austin, *Amer. J. Science,* (4), **14,** 156, 1902.

[4] O. R. Sweeney and G. N. Quam (*Journ. Amer. Chem. Soc.,* **46,** 958, 1924) describe permanent filter mats of powdered porcelain.

[5] E. Murmann (*Monats.,* **19,** 403, 1898) has described a modified Gooch crucible in which the precipitate can be dried and heated in a current of gas—*e.g.* lead sulphate, barium sulphate, zinc, manganese, copper and antimony sulphides. They are rather expensive and fragile.

A more recent modification of the Gooch crucible is a glass crucible into which is fused a sintered filter disc of finely powdered and sieved glass of various degrees of fineness.[1] It is claimed that such crucibles filter more rapidly, dry more readily, and show less variation in weight, when left exposed to the air, than do the standard Gooch crucibles. They are cleaned for re-use similarly to Munroe's crucible—see below. Naturally, this type of crucible cannot be heated to redness, nor will it stand the action of strong alkalies.

§ 51. Gooch Crucibles Packed with Platinum Felt—Munroe's Crucible.

C. E. Munroe[2] proposed platinum sponge in place of the asbestos in Gooch crucibles, and crucibles so packed have many applications not possible with the asbestos-packed crucibles.

1. *Preparation of the Platinum Felt.* A concentrated solution of chloroplatinic acid is treated with ammonium chloride in slight excess. The resulting precipitate of ammonium platinichloride is washed several times with water and finally with alcohol. The excess of alcohol is poured off as soon as the ammonium platinichloride has settled.

2. *Packing the Crucible.*—A perforated platinum crucible, with small and numerous holes, is placed upon several layers of filter-paper, and pressed firmly on the paper while the alcohol-moist mass of ammonium platinichloride is poured in until it is filled, say, to a height of 0·25 or 0·5 cm.[3] The alcohol will be rapidly absorbed by the filter-paper upon which the crucible is being pressed, and at the end of a few moments the surface of the salt in the crucible will suddenly appear "dry," showing that the excess of alcohol has been absorbed by the filter-paper. The crucible is then removed from the filter-paper, and a uniform layer of ammonium platinichloride should cover the bottom of the crucible. The crucible is warmed in a steam oven until the alcohol has all volatilised. The cover is placed on the crucible and the latter gradually warmed until the ammonium platinichloride has all decomposed. The temperature may then be raised to dull redness. The crucible is allowed to cool.

The bottom of the crucible should be covered with a continuous and uniform layer of platinum sponge, but generally the sponge will be found to have withdrawn, more or less, from the sides of the crucible, and to be interrupted by several cracks. Press the mass gently with the finger, or with a glass rod with a flattened end, so that the cracks are pressed together and a continuous

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[1] G. F. Hüttig, *Zeit. angew. Chem.*, **37**, 48, 1924; P. H. Prausnitz, *Analyst*, **50**, 440, 1925; *Chem. Ztg.*, **53**, 935, 955, 1929; *Arch. Pharm.*, **268**, 170, 1930; *Brit. Pat.*, Nos. 182, 218, 226, 286, 1924; J. Prescher and R. Claus, *Zeit. Unters. Nahr. Genussm.*, **50**, 420, 1925; R. H. Simon, *Journ. Assoc. Official Agr. Chem.*, **12**, 209, 1929; E. Cattelain, *Ann. Falsif.*, **23**, 301, 1930; W. F. Bruce and H. E. Bent, *Journ. Amer. Chem. Soc.*, **53**, 990, 1931.

[2] C. E. Munroe, *Journ. Anal. App. Chem.*, **2**, 241, 1888; *Chem. News*, **58**, 101, 1888; H. Neubauer, *Zeit. anal. Chem.*, **39**, 501, 1900; W. C. Heraeus, *Zeit. angew. Chem.*, **13**, 745, 1900; P. Bernhardt, *Chem. Ztg.*, **32**, 1227, 1908; O. Brunck, *ib.*, **33**, 649, 1909; W. O. Snelling, *Chem. News*, **99**, 229, 1909; *Journ. Amer. Chem. Soc.*, **31**, 456, 1909; O. D. Swett, *ib.*, **31**, 928, 1909; T. W. Richards and A. Staehler, *ib.*, **29**, 623, 1907; F. Zerban and W. P. Naquin, *ib.*, **30**, 1456, 1908; F. A. Gooch and F. B. Bayer, *Amer. J. Science*, (4), **25**, 249, 1908; M. M. Brewer, *George Washington Univ. Bull.*, **5**, 79, 1906; *Chem. Eng.*, **5**, 261, 1906; H. J. F. de Vries, *Chem. Weekblad*, **6**, 816, 1909. The main objection to Munroe's crucible is its cost—the platinum felt is packed in a platinum crucible; but O. Brunck (*Chem. Ztg.*, **33**, 649, 1909) has made a similar crucible with Royal Berlin porcelain, and "burned" the felt into the glaze so that it cannot be detached without the application of force, or overfiring. Brunck's crucible will bear a red heat if the temperature be raised gradually.

[3] Snelling recommends placing a circular piece of fine platinum wire gauze of suitable size in the bottom of the crucible before pouring in the ammonium platinichloride. The felt is then tougher and less easily injured, and also less liable to crack and curl.

layer of the platinum sponge is spread over the bottom of the crucible. If, however, the layer is not quite continuous, use more ammonium platinichloride to fill up the cracks and to patch the layer of platinum sponge. The cracks may be so bad that it is advisable to remove the platinum sponge by means of a spatula, and start again. When the crucible is covered with a uniform layer of platinum sponge, it is ready for use.[1]

Munroe recommends rubbing the platinum sponge with a glass rod at this stage in order to smooth out the mat and remove cracks. This compresses the mat and burnishes its surface. By gently rubbing all parts of the mat until the surface becomes considerably burnished, the smooth, polished surface so obtained has many advantages, even though the porosity of the felt is greatly reduced.

The felt prepared by the above directions, due to Snelling, is said to be 100 times more porous than one of asbestos. It also retains the finest precipitates without the difficulties of turbid filtrates or clogging of the felt presented by asbestos felt in filtering barium sulphate and calcium oxalate. There is also no danger of contaminating the filtrate with silica, alumina, iron oxide, magnesia and lime, as is the case with asbestos felt. The crucible is used for filtering and washing, like the regular Gooch crucible.

One special advantage of Munroe's crucible is that the precipitate can be removed by means of appropriate solvents and the crucible dried and weighed ready for the next determination.

In illustration, the following results may be quoted from Munroe's paper:—

	Grms.
Platinum crucible alone	30·6744
Crucible and felt, first ignition	31·0607
Crucible and felt, second ignition	31·0607
Crucible and felt, third ignition	31·0607
Crucible, felt and calcium oxalate	31·5385
The same after treatment with HCl, etc. . . .	31·0609
Second treatment with hydrochloric acid . . .	31·0608
Crucible, felt and barium sulphate	31·4403
After treatment with conc. H_2SO_4	31·0640
Second treatment with conc. H_2SO_4 . . .	31·0609

The crucible can be used over and over again for hundreds of analyses, unless careless handling makes the introduction of a new felt necessary. After weighing, the crucible is inverted to remove part of the precipitate, and the remainder is removed by placing the crucible on a pipeclay triangle over a porcelain dish so that the bottom of the crucible is immersed in the given solvent. By gradually heating the solvent, not to boiling, the precipitate will soon dissolve. Care must be taken with carbonates, or effervescence may cause particles of the felt to be dislodged.[2]

A list of solvents for various precipitates, taken from Swett's paper, is given in Table LXVIII., page 773.

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[1] Snelling recommends the addition of two or three drops of chloroplatinic acid to the platinum felt in the crucible. The porosity of the felt will cause the solution to distribute itself throughout the whole mass. On ignition, the chloroplatinic acid will be decomposed with the separation of platinum. The platinum which is so formed appears to cement the particles of platinum sponge together and to the walls of the crucible, so that the felted mass is toughened.

[2] Precipitates sometimes cling tenaciously to the surface of the platinum felt, and if they are removed mechanically, will often take particles of felt with them. In cases where it may be necessary to remove precipitates mechanically, a perforated disc of platinum of suitable size may be placed on top of the platinum felt, as recommended by Richards and Staehler (l.c.).

CHAPTER VI.

HEATING AND DRYING.

§ 52. Heating.

Bunsen Burner. --Prior to 1852, spirit lamps were in common use, but about this time R. W. Bunsen invented his famous burner.[1] The early instrument was faulty, but it was soon improved and appeared virtually in its present form in 1854. This burner, fig. 97, is the best type for general purposes. It is too well known to need any description.[2] There are a number of modifications, among which Teclu's burner [3] (fig. 104) is a useful type. It can give a rather higher temperature than the original form of Bunsen's burner. The gas and air can be regulated so as to give anything between a luminous smoky flame and a "blowpipe" flame. The latter will decompose calcium carbonate. Porcelain Bunsen burners (fig. 118) are convenient for use in hoods where metal burners would be corroded by the fumes.

Accessories for Bunsen Burners.—A large variety of accessories is listed in dealers' catalogues, each of which adapts the normal burner for some special purpose. For general laboratory work probably the two most useful accessories are the support carrying the frustum of a copper cone to protect the flame from draughts (figs. 98 and 139) and the mushroom head (fig. 120). The latter is particularly useful for charring filter-papers and for low-temperature ignition; it has not received the recognition it deserves.

Argand Burner. -- This type of burner is provided with a steatite jet and a metal or mica chimney (fig. 74). It serves much the same purpose as a Bunsen burner with a mushroom head and is specially useful where uniformity of temperature is needed. The so-called "micro-burners" are useful sources of heat when a bath is to be heated to a low temperature for a long time, and when a comparatively low uniform temperature is desired. See fig. 152, page 722.

Méker Burners.—G. Méker's burners [4] are probably the best high-temperature burners on the market. They can be obtained with or without a blast attachment (figs. 59 and 60). The blast Méker burner is quite satisfactory for

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[1] It appears to be mentioned first in a paper by R. W. Bunsen and H. E. Roscoe, *Pogg. Ann.*, **100**, 84, 1857; P. Desaga, *Dingler's Journ.*, **113**, 340, 1857; A. Kistner, *Chem. App.*, **2**, 185, 1915. For the efficiency of Bunsen burners, see H. O'Connor, *Chem. Trade Journ.*, **51**, 461, 1912.

[2] The burners are usually attached to the supply nozzle by means of rubber tubing. A drop of glycerol between the rubber and the metal will prevent the rubber sticking fast—A. H. Church, *Chem. News*, **35**, 1, 1877.

[3] N. Teclu, *Zeit. anal. Chem.*, **31**, 429, 1892; **33**, 450, 1894; *Journ. prakt. Chem.*, (2), **45**, 281, 1892; (2), **47**, 535, 1893. For a hot air Teclu burner, see P. Verbeck, *Chem. Ztg.*, **39**, 948, 1915.

[4] G. Méker, *Zeit. Beleuchtungswesen*, **11**, 196, 1905; *Bull. Soc. chim.*, (3), **33**, 210, 1905; *Chem. News*, **99**, 88, 1909; C. G. Fischer, *Met. Chem. Eng.*, **9**, 222, 1911.

silica and other ignitions requiring a blast.[1]   Méker burners are also adapted for heating muffles, and for crucible furnaces.   There are many advantages in making ignitions in muffles when a large number has to be made.

Hot-Plates. — Sand baths are convenient for heating round-bottomed vessels, but they are dirty at best, and they should be banished from analytical laboratories.   Silica plates or plates of asbestos millboard are frequently used, but the asbestos soon deteriorates where the flame strikes.   Silica plates are more economical, since they last a long time.[2]   Plates of cast iron, or boiler plate,[3] about 0·5 cm. thick, resting on a tripod or quadripod, and heated by a ring or a Fletcher's burner, are preferable to the sand bath.[4]

Radiator.-- When a liquid is to be evaporated or a moist solid is to be heated in a crucible, to avoid spattering it is generally safer to heat the crucible in a so-called "radiator," rather than on a hot-plate.   The "radiator" corresponds with the "nickel beaker" of Jannasch.[5]   The most convenient form of radiator is a nickel crucible with a triangle placed inside, so arranged that the crucible to be heated is approximately equidistant from the sides and bottom of the nickel crucible.   The nickel crucible and contents are heated over a small flame, when the liquid in the inner crucible is soon evaporated. The lid can then be placed on the nickel crucible and the contents of the inner crucible baked at a higher temperature.   Several modifications naturally suggest themselves.

Electric Heating.—If electric current is available, a great deal of the heating may be done more cheaply and cleanly than with gas.   Electricity is the ideal heating agent for a laboratory.   Hot-plates, air and water baths, hot-jacketed funnels and muffles can all be conveniently heated by electricity.

Triangles and Tongs.-–Plain pipeclay, porcelain or silica triangles with iron, or better, nickel or nichrome [6] wire are used for general work.   Silica triangles are best for high-temperature work; they are far more durable than porcelain or pipeclay, and better resist sudden changes of temperature.   Plain platinum triangles can be used for platinum crucibles.   They must be made of stout platinum wire and this is costly.   If a platinum crucible be blasted on a platinum triangle, the triangle may stick to the crucible.   The two can only be separated by tearing a piece out of the crucible.   Hence, it is better to use fused silica triangles for platinum crucibles which are to be blasted.

Hot platinum crucibles must not be lifted with iron, nickel or brass tongs in such a way that these metals come in contact with the hot platinum.   Brass or gunmetal tongs with a pair of platinum shoes over the tips are generally used.   If the tongs be placed on the bench points downwards after holding a hot crucible, the hot points are liable to pick up matter from the bench, which is afterwards transferred to the crucible.

[1] The blast gas burner was devised by R. W. Bunsen about 1854, and improved by E. H. Baumhauer (*Liebig's Ann.*, **90**, 21, 1854; P. Hart, *Chem. Gaz.*, **5**, 1, 1855).

[2] E. Erlenmeyer, *Zeit. Chem. Pharm.*, **8**, 639, 1864; C. Weigelt, *Repertm. Anal. Chem.*, **1**, 9, 1881.

[3] Cast iron is less inclined to warp than wrought iron.—E. D. Campbell, *Journ. Amer. Chem. Soc.*, **29**, 283, 1907.

[4] Nickel wire gauze, it may be added, does not "rust or perish" to the extent that other gauzes do.—H. L. Robinson, *Chem. News*, **76**, 253, 1897.

[5] P. Jannasch, *Praktischer Leitfaden der Gewichtsanalyse*, Leipzig, 37, 1904; W. M. Thornton, *Journ. Ind. Eng. Chem.*, **3**, 418, 1911; F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Berlin, 24, 1911; W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **700**, 33, 1919; A. C. Vournasos, *Zeit. anal. Chem.*, **53**, 175, 1914.

[6] R. C. Benner (*Eng. Min. Journ.*, **91**, 360, 1911) prefers nichrome wire—that is, an alloy of chromium and nickel—since it does not oxidise so readily in the blast burner.   Von Heygendorff (*Chem. Ztg.*, **35**, 523, 1911; A. Kette, *ib.*, **29**, 1208, 1905) uses pipeclay beads instead of clay tubes.

§ 53. Platinum Apparatus.

Modern platinum ware is apt to be inferior in quality to that on the market some years ago, and the cause was the subject of special inquiry by a committee of the American Chemical Society.[1] The main objections are: "(1) undue loss of weight on ignition; (2) undue loss in weight on acid treatment, especially after strong ignition; (3) unsightly appearance of the surface after strong ignition, especially after the initial stages of heating; (4) adhesion of crucibles and dishes to triangles sometimes to such an extent as to leave an indentation on the vessel at the points of contact with the triangle, even when complete cooling has been reached before the two are separated; (5) alkalinity of the surface of the ware after strong ignition; (6) blistering; and (7) development of cracks after continued heating." It is the general opinion that the trouble arises from the working of scrap platinum into chemical ware. The main difficulties here mentioned are not characteristic of platinum ware from some of the best manufacturers.

Many new and old platinum crucibles lose weight on long blasting. This is generally thought to be due to the distillation of iridium from the platinum alloy.[2] If a crucible suffers from this disease, the rate of loss per five minutes' blasting must be determined, and an allowance made. Beilstein[3] states that the loss in weight becomes less after repeated ignition. On the other hand, Hall[4] found the loss on the twentieth heating even greater than the first. The following numbers represent the loss in weight which a new platinum crucible suffered after successive half-hour ignitions on a blast. The weight of the new crucible was 22·5299 grms.:

$$0\cdot0005;\ \ 0\cdot0004;\ \ 0\cdot0003;\ \ 0\cdot0002;\ \ 0\cdot0001\ \text{grm.}$$

After a month's use, the crucible remained practically constant in weight during the same period of blasting.[5] Another crucible did not show this phenomenon, but seemed to lose steadily about 0·0003 grm. per half an hour's blasting. The only inference to be drawn from these discordant observations is that the alloys used for making different crucibles are not the same. With luck, crucibles can be obtained which undergo practically no loss when heated in the blast. Crucibles which suffer a change in the rate of loss with time must have the correction determined at frequent intervals. If a crucible loses 0·2 mgrm. on ten minutes' blasting, the necessary correction is obvious. It is sometimes convenient to take the weight of the crucible after the ignition.

Although platinum is not oxidised nor seriously attacked by the single acids

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[1] "Preliminary Report of the Committee on the Quality of Platinum Utensils," *Ind. Eng. Chem.*, 3, 986, 1911; 6, 512, 1914; G. K. Burgess and P. D. Sale, *ib.*, 6, 452, 1914; 7, 561, 1915; G. K. Burgess and R. G. Waltenberg, *ib.*, 8, 487, 1916.

[2] L. L. de Koninck, *Zeit. anal. Chem.*, 18, 569, 1879. H. Kayser (*Wied. Ann.*, 34, 607, 1888) noticed that platinum lost weight when heated in tubes in a current of air, and assumed that the platinum gave up fine particles to the air. L. Elsner (*Journ. prakt. Chem.*, (1), 99, 257, 1866) found platinum crucibles lost weight when heated in porcelain ovens. E. Sonstadt, *Chem. News*, 13, 145, 1866; G. A. Hulett and H. W. Berger, *Journ. Amer. Chem. Soc.*, 26, 1512, 1904; E. Goldstein, *Ber.*, 37, 4147, 1904; A. F. Joseph and W. N. Rae, *Journ. Chem. Soc.*, 111, 200, 1917; G. K. Burgess and P. D. Sale, *Journ. Wash. Acad. Sci.*, 5, 378, 1915. G. C. Wittstein (*Dingler's Journ.*, 179, 299, 1866) referred the loss to osmium, but F. Stolba (*ib.*, 198, 177, 1870) pointed out that the loss of weight is greater than the amount of osmium in the platinum ore. For the use of "palau" crucibles (gold 4 parts and palladium 1 part), see H. S. Washington, *Journ. Wash. Acad. Sci.*, 11, 9, 1921.

[3] F. Beilstein, *Pharm. Zeit. Russland*, 19, 630, 1880.

[4] R. W. Hall, *Journ. Amer. Chem. Soc.*, 22, 494, 1900.

[5] The lid of this crucible contained about 1·5 per cent. of iridium.

used in analytical chemistry, many substances attack and combine with platinum at comparatively low temperatures.[1]

The more important precautions to be considered in using platinum vessels may be conveniently summarised in the following decalogue:—

1. Do not heat "unknown" substances in platinum vessels.

2. Always keep the platinum ware bright and clean. For this purpose use fine sea sand, with rounded grains and free from grit, as a polishing powder.[2] This removes most impurities and polishes without serious loss. Apply the sand with the finger. Gmelin's recommendation to fuse a little potassium bisulphate in the crucible is a good method for cleaning the inside of badly tarnished crucibles.[3] The bisulphate is poured out of the crucibles while fluid, and the crucibles then cleaned with water and sand.

3. Never heat the platinum crucible or dish in contact with iron or metals other than platinum; nor let hot platinum be placed in contact with foreign metals. Use only pipeclay, silica or platinum triangles and platinum-shod tongs.[4]

4. Do not fuse metals in a platinum crucible, nor heat in the crucible salts of the easily reducible metals, particularly salts of lead,[5] silver, arsenic, antimony, copper, bismuth and tin. See page 264.

5. Do not heat phosphides nor the sulphides of the metals in platinum crucibles. Sulphur alone has no action.[6] Phosphorus attacks platinum. Phosphates, under reducing conditions, may form phosphides and phosphorus, which attack the metal.

6. Alkali carbonates do not attack platinum very much, but the attack by caustic alkalies and alkaline earths is serious — particularly lithium and barium oxides. Hence, alkali nitrates, nitrites, hydroxides and cyanides should not be heated in contact with platinum, if it can be avoided.

7. Do not use aqua regia or free chlorine in contact with platinum. Watch

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[1] For the corrosion of platinum by ammonium and potassium bromoplatinates, see G. Méker, *Compt. rend.*, 125, 1029, 1897; *Chem. News*, 77, 19, 1898; by potassium bisulphate, see page 168; by borax and boric acid and by ferric chloride ($4FeCl_3 + Pt = PtCl_4 + 4FeCl_2$), see A. Béchamp and C. Saint Pierre, *Compt. rend.*, 52, 757, 1861; *Chem. News*, 4, 284, 1861; by ignition of ammonium chloroplatinate, see F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, 2, 225, 1910; by solutions of titanic hydroxide in the presence of nitric or sulphuric acid, see H. Rose, *Traité Complet de Chimie Analytique*, Paris, 1, 1028, 1859; W. B. Giles, *Chem. News*, 99, 4, 1909; by sulphuric acid, A. Scheurer-Kestner, *Compt. rend*, 91, 59, 1880; 86, 1082, 1878; *Bull. Soc. chim.*, (2), 24, 501, 1875; (2), 30, 28, 1878; M. Delépine, *Compt. rend.*, 141, 886, 1013, 1905; *Chem. News*, 93, 108, 120, 1906; L. Quennessen, *ib.*, 93, 271, 1906; *Compt. rend.*, 142, 1341, 1906; J. T. Conroy, *Journ. Soc. Chem. Ind.*, 22, 465, 1903; L. R. W. M'Cay, *Inter. Cong. App. Chem.*, 8, 351, 1912; G. K. Burgess and P. D. Sale, *Bull. Bur. Standards*, 12, 289, 1916; by sodium carbonate, see page 144; by selenium compounds, page 483; and by nitric acid, G. P. Baxter and F. L. Groves, *Journ. Amer. Chem. Soc.*, 36, 1089, 1914.

[2] F. Stolba (*Dingler's Journ.*, 198, 178, 1870) says good sand for the purpose may be obtained by shaking dried sponges.

[3] If outside, put the bisulphate in a dish of suitable size, and allow the flux to envelop completely the vessel to be cleaned. F. Winkle (*Chem. Ztg.*, 23, 803, 1899) recommends borax instead of potassium bisulphate for crucibles stained by the ignition of plant ashes. F. Stolba (*Dingler's Journ.*, 221, 135, 1877) cleans dirty crucibles by melting equal parts of boron fluoride and boric acid in the crucible. C. D. Manzoff (*Ann. Chim. anal.*, 18, 316, 1913) cleans off spots by fusing a mixture of sodium carbonate and borax (2 : 1) and afterwards washing off with water.

[4] Sodium amalgam is useful for cleaning platinum stained with foreign metals (*Chem. News*, 2, 286, 1860). The amalgam is gently rubbed on the platinum with a cloth, and then moistened with water. This oxidises the sodium, and leaves the mercury free to amalgamate with the foreign metals. The mercury is wiped off, and the crucible cleaned with sand.

[5] Unfortunately, we sometimes have to take risks; but never if it can be avoided.

[6] W. C. Heraeus and W. Geibel, *Zeit. angew. Chem.*, 20, 1892, 1907.

for reactions in which chlorine might be liberated, *e.g.* hydrochloric acid and oxidising agents. A moment of thoughtlessness may render it necessary to purchase a new crucible.

8. Direct contact of platinum with burning charcoal, coal or coke must be avoided. The platinum becomes brittle and liable to fracture if this precaution be neglected.[1]

9. Never let a smoky flame come in contact with platinum, since a grey film [2] is formed on the platinum in mild cases, and the platinum is quite disintegrated in bad cases. For a similar reason, do not let the inner cone of a Bunsen flame come in contact with the metal.[3]

10. Platinum is easily bent,[4] and care must be taken not to bend the crucible in handling or gripping with the tongs.[5]

§ 54. Desiccators.

Various forms of desiccators are on the market and of these the Scheibler patterns, either for air drying or drying *in vacuo*, are as convenient as any for general use.[6]

There is a fault with these desiccators. Moist air is lighter than dry air. Hence, it is bad on principle to place the desiccating agent at the bottom of the desiccator, beneath the substance to be dried. The action is then dependent upon the slow diffusion of the lighter moist air downwards. Hempel [7] devised a desiccator in which the drying agent is placed above the substance to be dried. The action is said to be more rapid because of the circulation induced by the natural tendency of the light moist air to accumulate in the upper part of the desiccator.[8] This argument clearly does not apply to drying *in vacuo*.

[1] P. Schützenberger and A. Colson, *Compt. rend.*, 94, 26, 1882; A. Colson, *ib.*, 94, 1710, 1882; 82, 591, 1876; J. Boussingault, *Ann. Chim. Phys.*, (2), 16, 5, 1821; C. L. Berthollet, *ib.*, (1), 67, 88, 1808; C. G. Memminger, *Amer. Chem. Journ.*, 7, 172, 1886; V. Meyer, *Chem. News*, 73, 235, 1896; A. B. Griffiths (*Chem. News*, 51, 97, 1885) says "platinum fuses at a comparatively low temperature when heated in contact with carbon."

[2] Another type of grey film is formed even when the platinum is only heated in an oxidising flame. O. L. Erdmann (*Journ. prakt. Chem.*, (1), 79, 117, 1860; *Chem. News*, 2, 256, 1860) showed that this film is due to a surface molecular change (crystallisation—W. Rosenhain, *Proc. Roy. Soc.*, 70, 252, 1902), and is not attended by a gain or loss of weight. The stain should always be scoured off as soon as it is formed, otherwise the devitrification is inclined to spread. Coal-gas, even at 600°, is injurious to platinum and forms a sooty layer containing the metal—F. Mylius and C. Hüttner, *Zeit. anorg. Chem.*, 95, 257, 1916.

[3] S. Kern (*Chem. News*, 35, 77, 1877) refers to the attack of platinum by the sulphur and carbon compounds in coal-gas. A. Rémont, *Bull. Soc. chim.*, (2), 35, 486, 1881. H. Petrzilka (*Zeit. angew. Chem.*, 7, 255, 1894) recommended a gilded platinum protective capsule to resist attack by smoky flames.

[4] A. A. Blair (*The Chemical Analysis of Iron*, Philadelphia, 33, 1908) recommends the use of a wooden mould to fit the inside of the crucible for straightening the crucible when it is bent. These can be purchased with the crucible and are of great use.

[5] For soldering and repairing crucibles, see J. W. Pratt, *Chem. News*, 51, 181, 1885; H. J. Seaman, *ib.*, 49, 274, 1884; T. Garside, *ib.*, 38, 65, 1878.

[6] For electrically-heated desiccators, see T. B. Robertson and C. L. A. Schmidt, *Journ. Biol. Chem.*, 27, 429, 1916.

[7] W. Hempel, *Ber.*, 23, 3566, 1890; *Zeit. angew. Chem.*, 4, 84, 200, 1891; F. Cochius, *Chem. Ztg.*, 24, 266, 1900; E. Biltz, *Pharm. Centr.*, 12, 353, 453, 1890. For the "ether" vacuum desiccator, F. G. Benedict and C. R. Manning, *Amer. Chem. Journ.*, 27, 340, 1902; H. C. Gore, *Journ. Amer. Chem. Soc.*, 28, 835, 1906; E. Douzard, *Amer. Journ. Pharm.*, 80, 588, 1908.

[8] There is also the objection that the air in the interior expands when a hot crucible is introduced. On cooling, a partial vacuum may be produced, which renders the removal of the lid difficult. Hence, some prefer a desiccator with a side tubulure in which is fitted a calcium chloride tube which provides for the free circulation of dry air.—A. R. Leeds, *Chem. News*, 23, 177, 1871.

The main objection to Hempel's desiccator is that, when sulphuric acid is used as the drying agent, the acid is apt to spill, particularly when the desiccator is being opened.

When the loss on ignition of certain clays is to be determined and the clays, after ignition, are cooled in the usual way, it is very difficult to get constant results. This is particularly noticeable when the blast is not very powerful. The difficulty is eliminated if the ignited clay be cooled *in vacuo*. The trouble arises from the fact that clays, dehydrated at a comparatively low temperature,
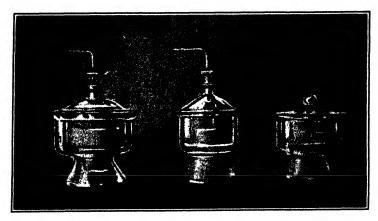
FIG. 34.—Desiccators.

adsorb the dry gases in an ordinary desiccator in a remarkable manner. As much as 1·5 per cent. may be so adsorbed.[1]

Granular calcium chloride and concentrated sulphuric acid are the commonest desiccating agents. Phosphorus pentoxide, alkali hydroxides, silica gel, magnesium perchlorate, barium oxide and anhydrous calcium sulphate [2] are also recommended. The drying agents require attention. The sulphuric acid should be frequently renewed, since that which has stood a long time in a desiccator is ineffective; [3] and, if it has become discoloured, owing to contamination with dust, sulphur dioxide may be given off (page 4), and this sometimes can be detected by its smell. Pumice soaked in concentrated sulphuric acid is excellent. Phosphorus pentoxide soon becomes ineffective owing to the glazing of the surface with metaphosphoric acid, and hence this agent is not used except in special circumstances. Fresh granulated calcium chloride is most useful for general work. Kral [4] prefers a mixture of calcium chloride and quicklime in place of calcium chloride alone.[5] Some forms of desiccators are shown in fig. 34.

[1] C. Friedel, *Compt. rend.*, **122**, 1006, 1896; *Bull. Soc. Min.*, **19**, 14, 94, 1896; **22**, 5, 84, 1899; J. W. Mellor and A. D. Holdcroft, *Trans. Cer. Soc.*, **10**, 94, 1911.

[2] For magnesium perchlorate, see H. H. Willard and C. F. Smith, *Journ. Amer. Chem. Soc.*, **44**, 2255, 1922; S. Lenher and G. B. Taylor, *Ind. Eng. Chem. Anal. Ed.*, **2**, 58, 1930; for barium oxide, see H. S. Booth and L. H. McIntyre, *Ind. Eng. Chem. Anal. Ed.*, **2**, 12, 1930; for anhydrous calcium sulphate, see W. A. Hammond and J. R. Withrow, *Ind. Eng. Chem.*, **25**, 653, 1112, 1933; for alumina, see F. M. G. Johnson, *Journ. Amer. Chem. Soc.*, **34**, 911, 1912.

[3] W. F. Hillebrand, *Amer. Chem. Journ.*, **14**, 6, 1892.

[4] H. Kral (*Pharm. Centr.*, **37**, 105, 1895) also recommends fused potassium bisulphate in place of sulphuric acid. The "spent" bisulphate can be regenerated by fusion.

[5] For the efficiency of desiccating agents, see R. Fresenius, *Zeit. anal. Chem.*, **4**, 177, 1865; C. Voit, *ib.*, **15**, 432, 1876; H. C. Dibbits, *ib.*, **15**, 121, 1876; P. A. Favre, *Ann. Chim. Phys.*,

§ 55. Laboratory Hoods, Fume Chambers.

In quantitative analysis, where a great many evaporations are conducted on a water-bath, it is necessary to protect the liquids from dust during the evaporation. The arrangement shown in fig. 62, page 148, is convenient for single evaporations,[1] but where many evaporations have to be made, special closets are advisable. In silicate analyses, great volumes of hydrochloric acid, steam and ammoniacal vapours are delivered into the atmosphere of the laboratory by evaporating liquids, and these vapours condense on the metal-work; this sets up rapid and serious corrosion. Hence, an efficient fume closet is necessary for accurate work, for protecting the health of the worker and for the preservation of apparatus in the laboratory. The comfort of the laboratory is largely determined by the efficiency of the hood.

The fume chamber must have an efficient draught independent of atmospheric conditions; and it must protect the exposed surface of evaporating liquids from dust.

The need for a vigorous draught is most emphasised in dealing with operations in which hydrofluoric acid vapours, hydrogen sulphide and other noxious vapours are evolved; while the need for protection from dust is most pronounced when liquids are evaporating in shallow basins. If a large volume of air be passing through the hood, the risk of contamination from dust may be greater than when the draught is less. Hence, it may be advisable to install two types of hood: one specially designed for vigorous draught and the other specially designed to prevent contamination from falling dust.

In the former type of hood—the fume closet—the chamber should be relatively small. A number of small hoods are more efficient than one large hood. The carrying capacity of the air for moisture and the draught of the hood are largely dependent upon the slight heating which the air receives in the chamber. In a large hood the warmed air is chilled and its carrying capacity for moisture is reduced, so that the fumes are not carried through the outlet provided, but work their way into the laboratory. The upper roof of the chamber should not taper too abruptly and, if possible, the exit flue should be vertical throughout its entire length, so that the rising air may be baffled as little as possible. The sectional area of the exit flue should be about one-third the floor area. For structural reasons it is not always convenient to provide a vertical flue. When the exit leads into a chimney, the hood usually draws well, but if the exit flue in the ground floor of a building be led through the outer wall, the hood may be quite useless against the "back draught" set up by an unfavourable wind. A fan is then a valuable auxiliary, since it makes the action of the hood independent of the weather. Sometimes a jet of compressed air blown into the hood just below the base and directed into the exit flue, on the principle of a steam ejector, is very efficient, and there is then very little trouble with corrosion, as is the case when a fan is used. A gas burner placed just below the base of the exit flue will sometimes provide

(3), **12**, 223, 1844; V. Regnault, *ib.*, (3), **15**, 129, 1845; J. D. van der Plaats, *Rec. Trav. chim.*, **6**, 45, 1889; E. G. Morley, *Amer. J. Science*, (3), **30**, 140, 1885; (3), **34**, 199, 1887; *Journ. Chem. Phys.*, **3**, 241, 1905; *Journ. Amer. Chem. Soc.*, **26**, 1171, 1904; G. P. Baxter and R. D. Warren, *ib.*, **33**, 340, 1911; G. P. Baxter and H. W. Starkweather, *ib.*, **38**, 2038, 1916; A. T. McPherson, *ib.*, **39**, 1317, 1917; M. V. Dover and J. W. Marden, *ib.*, **39**, 1609, 1917; J. W. Marden and V. Elliott, *Ind. Eng. Chem.*, **7**, 320, 1915; J. H. Bower, *U.S. Bur. Standards Journ. Research*, **12**, 241, 1934.

[1] C. Winkler, *Ber.*, **21**, 3563, 1888; W. Hempel, *ib.*, **18**, 1434, 1885; C. M. Stewart, *Chem. News*, **52**, 208, 1885; C. R. McCabe, *Chem. Eng.*, **12**, 182, 1910; Spectator, *Chem. Ztg.*, **35**, 254, 1911.

sufficient draught. The hood illustrated in fig. 35 is typical of a good fume closet.

For evaporating chambers a particularly vigorous draught is not needed, because the passage of a large volume of air over the surface of an evaporating
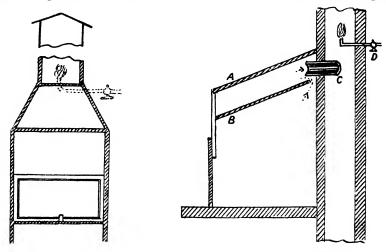
FIG. 35.—Front of Fume Chamber.   FIG. 36.—Treadwell's Flue.

liquid may lead to the deposition of dust from the air on the liquid. If there is too little draught, the crystallising salts may "creep" badly and the vapours will work back into the laboratory. There is also a risk of contamination from dirt falling down the exit flue, particularly on windy days. Hence, the exit flue of an evaporating chamber should not lead directly into a chimney.[1] Fresenius recommends leading the exit flue into a separate Russian chimney. "No fire must ever be made under this chimney, but it is most desirable to have this chimney placed close to another chimney kept constantly warm." Treadwell recommends the arrangement illustrated in fig. 36, where a kind of "dust trap" prevents the passage of dust into the evaporating chamber when a "back draught" occurs on a windy day. The hood has a glass roof A and about 15 cm. below is a second glass plate B, which comes within 3 cm. of the inner wall of the hood throughout its whole length. Between the two glass plates is a clay pipe C, 15 cm. long and 5 cm. diameter, placed above the inner edge of the lower glass plate, and leading into the chimney in which a small gas flame D is burning. Dust, sand and dirt from the chimney "falls upon the plate B; none gets into the hood."

[1] R. Fresenius, *Quantitative Chemical Analysis*, London, 1, 62, 1876; F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, 2, 26, 1911; H. S. Sherman, *Chem. Eng.*, 11, 21, 1910; C. R. McCabe, *ib.*, 12, 183, 1910; E. Keller, *Ind. Eng. Chem.*, 2, 246, 1910; C. F. Mabery, *Journ. Anal. App. Chem.*, 6, 247, 1892; J. K. Meade, *The Design and Equipment of Small Chemical Laboratories*, Chicago, 1908; T. H. Russell, *The Planning and Fitting-up of Chemical and Physical Laboratories*, London, 41, 1903; C. R. Hoover in *A Report . . . On the Construction and Equipment of Chemical Laboratories*, New York, 69, 1930. For contamination by paint from inside of hood, see A. Schaeffer, *Zeit. Nahr. Genuss.*, 24, 403, 1912.

CHAPTER VII.

PULVERISATION AND GRINDING.

§ 56. Pulverising Large Quantities.

THERE is no difficulty in reducing friable materials to powder in, say, porcelain mortars, but harder substances present some difficulty. It is almost impossible to pulverise hard, tough substances without some contamination from the crushing or grinding apparatus. For sampling, and for other experimental purposes, the breaking of stone, in bulk, down to particles, say 10's lawn, is commonly done in a crusher. Braun's jaw crusher [1]—fig. 37—is useful for crushing a large quantity of material. This machine reduces the material between a pair of jaws, one of which is stationary and the other vibratory. The fineness of the grinding is regulated by opening or closing the jaws by a regulating screw. The jaws can be adjusted to crush material from a diameter of $2\frac{1}{2}$ in. to that which will pass a 10's lawn. For fine crushing, however, the material is best run through, at least, twice —once with the jaws comparatively wide apart, the second time with the jaws close
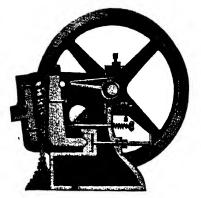
FIG. 37.—Braun's Jaw Crusher.

together. The machine is run at about 200 revolutions per minute. It can be operated by power or hand. It should be perfectly clean before it is used.

In Braun's disc pulveriser the material is pulverised between a pair of iron discs. A small machine will reduce 80 to 90 lbs. of material from $\frac{1}{4}$-in. mesh to 10's lawn per hour. It may also be run by power or hand. There is always a tendency to contamination from the iron disc of the pulveriser or the steel jaws of the crusher. Hence the sample for analysis should be very carefully magneted if it has been passed through the jaw or disc crushers. The worn parts of either of the above machines are made interchangeable and consequently repairs are easy.

§ 57. Pulverising Small Quantities.

Large lumps may be broken into coarse powder [2] by wrapping a lump in several folds of writing paper and striking it sharply with a hammer while it is

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[1] F. W. Braun, *U.S. Pat. No.* 497802, 1902; K. Zulkowsky, *Zeit. anal. Chem.*, 27, 24, 1888.

[2] If there are no objections, many minerals (*e.g.* felspar, flint), difficult to pulverise, become quite brittle if calcined and suddenly quenched in cold water.

resting on a steel plate placed upon a firm, solid support.   The coarse fragments so obtained can be still further reduced on a hard steel plate (a, fig. 38), on which is placed a steel cylindrical ring b.   A hard steel pestle c fits into the ring. The steel pestle and plate are made from the hardest "diamond" steel—hence the term "diamond mortar." [1]   The fragment of rock to be pulverised is placed on the steel plate within the ring.   The plate is placed on a firm support.   The pestle is depressed by a few sharp blows with a mallet.   Care must be taken not to grind or rub the metals against the fragments, otherwise the risk of contamination is greater.   This is the case, for example, with the mortar of the type shown in fig. 39, which is made from the very best hardened tool steel, and is useful for breaking hard rocks.   Most materials can be magneted after crushing so as to remove steel particles introduced during crushing.

The magneting of a ground powder to remove fragments of iron from the crusher is conveniently done by means of an electro-magnet.   A certain

FIG. 38.—Abich's Mortar and Pestle.   FIG. 39.—Steel Mortar and Pestle.

amount of discretion is needed, because, not only is iron derived from the crushing apparatus withdrawn, but certain magnetic minerals—magnetite, for example—may be removed at the same time.   With the more powerful electromagnets, minerals which are sometimes considered to be non-magnetic [2]— limonite, hematite, chromite, iron and copper pyrites—may be removed.   This occurs with the more powerful electro-magnets which have their poles tapering to blunt points and with the points close together.   Hence, false results would be obtained in the analysis of certain materials if the powdered sample were first magneted by such instruments.

When the substance under investigation itself contains magnetic materials, *e.g.* magnetic oxide of iron, magneting is not admissible, even though it is practically impossible to crush large or small quantities of hard material in iron vessels without contamination of iron.   Hence, the iron determination must necessarily be high.

The material should be crushed fine enough to allow it to be ground in an agate mortar without the particles flying off during grinding.   Care must also be taken to grind all the sample in this way, otherwise the harder fragments may be unconsciously rejected and the softer particles alone retained for examination. [3]

[1] Also called Abich's steel mortar, although it was not devised by H. Abich (*Pogg. Ann.*, **23**, 309, 1831).   W. I. Iwanoff, *Journ. Russ. Phys. Chem. Soc.*, **34**, 397, 1902.

[2] But which are in reality feebly magnetic—M. Faraday, *Phil. Trans.*, **153**, 1, 43, 1846; C. G. Gunther, *Electro-magnetic Ore Separation*, New York, 1909.

[3] For errors in the analysis of iron pyrites due to grinding with Wedgwood-ware mortars and pestles, see N. Glendinning and A. J. M. Edgar, *Chem. News*, **27**, 13, 1873.

§ 58. Grinding in Agate Mortars.

An agate mortar and pestle are commonly used for fine grinding. The mortar and pestle should be selected with care. They should be free from cracks and indentations. It is always necessary to be on guard against contamination from the grinding apparatus. Cracks and soft seams in an agate pestle and mortar are a source of danger. The small agate mortars and pestles are usually too short to hold with comfort. They should be fitted in wooden handles and bases (fig. 40). Beginners most frequently err in charging the mortar with too much material. It is best to grind the material in small portions at a time until sufficient is obtained for the analysis.
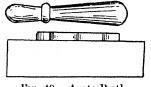
Fig. 40.—Agate Pestle and Mortar.

When large quantities of material have to be ground, an agate mortar and pestle driven by power can be used. Carling's instrument is superior to M'Kenna's.[1] These machines work automatically and with but little attention. The motions of the agate pestle and mortar simulate hand-grinding. In Carling's instrument, fig. 41, the table holding the mortar is rotated by a worm and worm wheel

Fig. 41.—Carling's Power-driven Agate Pestle and Mortar.

in the pedestal. This is driven by a chain band in the base. The pestle is worked by an eccentric movement on the rotating mortar.

As a rule, a power-driven agate mortar and pestle wears more rapidly than one used for hand-grinding. The speed must not be great enough to project the powder over the sides of the mortar. The driving wheel should run at

[1] K. Zulkowsky, *Ber.*, **20**, 2664, 1887; C. T. M'Kenna, *Eng. Min. Journ.*, **70**, 462, 1900; *Iron Age*, **66**, 9, 1900; W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **700**, 62, 1919; J. W. Mellor, *Trans. Cer. Soc.*, **10**, 94, 1911.

100 to 150 revolutions per minute. The materials in the mortar must be protected from contamination by oil from the wheels and gearing. A copper cup may be attached to the handle of the pestle, and a rubber sheet wrapped round the axle to reduce the risk of contamination from oil on axles and wheels above the mortar. The machine can also be advantageously run in a glass case to protect the contents of the mortar from dust.

§ 59. The Dangers of Fine Grinding.

There are a few risks incidental to the operation of grinding which must be noticed. Fine grinding is not to be applied indiscriminately. It must not be assumed that the powders ground specially fine for, say, Smith's process for alkalies, for the determination of ferrous iron, for carbonate fusions, have the same properties as coarse powders. The more important effects of fine grinding on the composition of a powder are as follows:—

1. *Contamination from the Grinding Apparatus.*—The finer the grinding the greater the risk of contamination from the grinding vessels and, in consequence, the greater the variation in the amount of silica and other constituents derived from the pestle and mortar.

Hempel[1] has investigated the effect of grinding 10 grms. of glass in mortars and pestles made of agate, steel and cast iron until the glass passed through a given sieve. The results are given in Table XIV.

Table XIV.—Influence of Grinding Apparatus on the Composition of a Powder.

Material.	Mortar.		Pestle.	
	Weight.	Loss in weight.	Weight.	Loss in weight.
Agate	371·741	0·041	44·242	0·011
Steel (new) . .	295·078	0·029	134·647	0·0021
Steel (old) . .	295·049	0·005	134·645	0·0004
Cast iron (new) . .	884·917	0·041	144·383	0·0009
Cast iron (old) . .	884·825	0·014	144·382	0·0000

This table shows that the loss in weight, and consequently also the contamination of the materials being ground, is greater with agate mortars and pestles. Hempel supposes that steel mortars and pestles are the best for grinding purposes; there is then less contamination. The *nature* of the contamination, however, presents a difficulty. Iron is one of the important impurities in clays and the analytical numbers for this impurity would be too uncertain if iron mortars and pestles were used for the grinding. The effect of the impurity derived from the agate has an inappreciable effect on the analytical numbers. It is therefore best to avoid, as much as possible, the use of the metal mortars and pestles and keep to agate.[2]

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[1] W. Hempel, *Zeit. angew. Chem.*, **14**, 843, 1901; G. A. James, *Chem. Eng.*, **14**, 380, 1911; V. Lenher, *Ind. Eng. Chem.*, **4**, 471, 1912; *Chem. News*, **106**, 183, 1912.

[2] H. Wurtz (*Amer. J. Science*, (2), **26**, 190, 1858) suggested removing the iron by digesting the powder with iodine water. A. Gautier (*Compt. rend.*, **131**, 647, 1276, 1900) was misled in his estimate of the amount of hydrogen occluded in granite by the contamination of the

2. *Gain and Loss of Hygroscopic Moisture.*—The fact that powders in "a very fine state of subdivision greedily absorb moisture from the air during the operation of weighing"[1] is well known. The speed of absorption is greater the finer the grinding. Thus, Day and Allen[2] have shown that coarsely ground felspar, containing little or no hygroscopic moisture, takes up progressively increasing amounts of moisture as the powder becomes finer, and the quantity so taken up may amount to 1 per cent. of the weight of the sample. Again, Hillebrand[3] found for a noritic rock the results indicated in Table XV.

Table XV.—Influence of Fineness of a Powder on Hygroscopicity.

Condition of rock.	Water.	
	Below 100°.	Over 100°.
60 apertures per cm. .	0·03	0·66
After 30 min. grinding	0·10	0·66
After 120 min. grinding	0·74	1·00

This all agrees with an old observation of Descharmes,[4] who showed that rock crystal (quartz) increased in weight on pulverisation to such an extent that the original weight might be doubled. Furthermore, Thugutt[5] has shown that some minerals take up water during fine grinding, while others—*e.g.* apophyllite—lose water. Hence, he infers that the hygroscopic moisture is best determined on a coarsely ground sample.

3. *Gain or Loss of Combined Water.*—Bleeker[6] has noticed that in grinding crystallised magnesium sulphate 2·55 per cent. of water was lost during two hours' grinding with a Wedgwood-ware pestle and mortar; disodium hydrogen phosphate lost 1·85 per cent.; potash alum, 0·49 per cent. With barium chloride there was an increase of 2·11 per cent. in weight. Steiger obtained similar results with calcium sulphate.

4. *Oxidation of Ferrous Compounds.*—Mauzelius[7] has shown that with minerals containing ferrous compounds quite an appreciable amount is oxidised to ferric oxide during fine grinding. Thus, 5·13 per cent. of ferrous oxide was obtained on a coarsely ground sample, and 3·13 per cent. on the same sample finely ground. It is therefore obvious that the powder must be ground as coarsely as possible—say 120's to 150's lawn—when the ferrous oxide is to be determined. The degree of coarseness is determined by the degree of decom-

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rock with iron during grinding. H. W. Hutchin (*Inst. Min. Met. Bull.*, 149, 1917) found that a sample of cassiterite uncrushed gave 75·1 per cent. of tin; if crushed in an agate mortar, 75·1 per cent.; in an iron mortar, 74·0 per cent.; and in different Wedgwood-ware mortars, 73·35, 73·65 and 72·95 per cent.

[1] R. W. Atkinson, *Chem. News*, 49, 217, 1884.
[2] A. L. Day and E. T. Allen, *Amer. J. Science*, (4), 19, 93, 1909.
[3] W. F. Hillebrand, *Journ. Amer. Chem. Soc.*, 30, 1120, 1908.
[4] P. Descharmes, *Recueil Industriel*, 1, 64, 1828.
[5] S. J. Thugutt, *Centr. Min.*, 677, 1909; F. von Kobell, *Journ. prakt. Chem.*, (1), 107, 150, 1869.
[6] J. B. Bleeker, *Chem. News*, 101, 30, 1910; C. E. Gillette, *ib.*, 104, 313, 1911.
[7] R. Mauzelius, *Sveriges Geol. Und. Arsbok*, 3, 1, 1907; N. Knight, *Chem. News*, 97, 122, 1908 (oxidation of siderite); G. Steiger, *Bull. U.S. Geol. Sur.*, 413, 33, 1910; E. T. Allen and J. Johnston, *Ind. Eng. Chem.*, 2, 196, 1910 (oxidation of pyrites).

position of the powder in 15 or 20 minutes by digestion with boiling hydrofluoric acid.[1]

Hillebrand has confirmed these observations, and tried grinding hard minerals under water and under alcohol, with the idea of cutting off oxygen from the powder during the grinding. Alcohol gave the better results. He showed that it was not merely increased surface which gave rise to the oxidation, but local heating of the grains in contact with the air at the moment of crushing. He therefore recommended the following procedure:—"The coarse powder is covered in the mortar with absolute alcohol that leaves no residue whatsoever on evaporation. The amount used should not be more than enough to form a very liquid emulsion during the operation of grinding. One or two additions of alcohol may be needed if the grinding has to be of long duration. The grinding should be continued in any case until the mass becomes somewhat thick, then the mortar and pestle are left to dry by unaided evaporation of the excess of alcohol; a wide glass tube should be supported above the mortar to keep out the dust without too much impeding air circulation. When supposed to be thoroughly dry, the powder is transferred in its entirety to a watch-glass and placed on the balance pan, where it is to be kept till it is quite evident that no further loss in weight takes place. It is then transferred to the sample tube." But even then, adds Hillebrand, "if a very fine powder must be employed, there seems no way known at present of correcting for whatever oxidation may have taken place during the grinding."

§ 60. Sieving, Lawning or Screening.

Ground materials are sieved or lawned to make sure that no particles above a certain maximum size are present. Great care must be taken that there be no
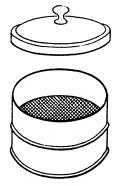
FIG. 42.—Lawn with Lid and Collecting Box.

contamination from the material of which the screens are made. Screens made of the same metal as one of the constituents to be determined are forbidden. Lawns made from brass, phosphor bronze and silk are in common use in analytical laboratories. Silk lawns are used whenever metallic contaminations are prohibited. Silk lawns are made from the best Italian silk mounted in wooden or metal frames, with or without collecting box and lid (fig. 42). The following are some commercial sizes of silk lawns:—23, 30, 46, 61, 76, 86, 117, 132, 147 apertures per linear inch. The powder should be gently shaken through these lawns in order to avoid contamination. The sieving of powders with silk lawns for the determination of ferrous oxide is condemned by many analysts (page 515), because of the possibility of contamination with silk fibres.

In sieving, *all* the powder must pass through the lawn. If only a portion be allowed to pass through, the "knottings" (*i.e.* the residue on the lawn) may have a different composition from that which has passed through. The more brittle constituents of a mixture—*e.g.* quartz and felspar—will be pulverised first. Thus, Zaleski[2] showed that the dust produced in pulverising granites is richer in felspar relative to quartz and the darker-coloured minerals than the coarser grains of the

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[1] If the single treatment does not effect complete decomposition, "which will often be the case" (Hillebrand), the solution, after titration, is allowed to settle, the residue washed once by decantation with water, and again treated with hydrofluoric acid.

[2] S. Zaleski, *Tschermak's Mitt.*, 14, 350, 1895.

powder; and with glassy frits, the parts which pulverise first are richer in alkali.[1] Hence, the residue on the lawns must be reground until all passes through.

It is generally advisable to state the size of the mesh of the lawn used in analytical and experimental work. There is some confusion owing to differences in the size of wire and method of weaving. In order that there might be as little confusion as possible, the Institute of Mining and Metallurgy have arranged a set of sieves with a definite size of aperture, as have also the United States Bureau of Standards and the British Standards Specification Committee.[2]

[1] T. E. Thorpe and C. Simmonds, *Proc. Manchester Lit. Phil. Soc.*, 45, 1, 1901; *Journ. Chem. Soc.*, 79, 791, 1901.

[2] *British Stand. Inst.*, Specification No. 410, 1931.

CHAPTER VIII.

SAMPLING.

When conscious choice is permitted to enter into the operation of sampling, a fair sample will not result, except by a miracle.—W. GLENN.

§ 61. The Problem of Sampling.

A FEW grams of material are sufficient for a chemical analysis, although tons of material may be bought or sold on the result. Large sums of money, too, may be involved in the results of experiments made with but a minute fraction of the total bulk of the material. In such cases it is of fundamental importance to work with samples typical of the whole, since a small error on a gram of material would be multiplied a millionfold when calculated up to tons. If the material be perfectly homogeneous, a "grab" sample, taken at random from any part, will be quite representative. In other cases—for instance, a clay bank, or a prospective clay field, or a cargo of bone for moisture, where the amount of moisture might vary from 3 to 13 per cent.—analyses and tests made on grab samples may be quite misleading. In sampling copper ore of medium grade, Dickenson[1] found the following differences expressed as a percentage of the copper content of the ore: Average difference between grab and mechanical sampling, 7·1; maximum difference between the results, 28·6; percentage of cases in which the grab sample was high, 55·0; percentage of results over 10 per cent. wrong, 30·0. Hence he concludes that the results obtained by grab sampling are "not only useless, but dangerously misleading."

Sampling is the art of extracting from a large bulk of material a small portion which shall fairly represent the character of the whole bulk. It would be difficult to over-emphasise the importance of accurate sampling.[2] Indeed, the errors incidental to the process of chemical analysis are sometimes insignificant when compared with the errors involved in bad sampling. It is surprising, to one who realises the importance of this subject, to contrast the care taken in conducting a chemical analysis with the carelessness which prevails in sampling. The analysis of a carelessly selected sample is worth nothing. Many complaints of the failure of chemical analyses can be traced to faulty sampling.

In sampling commercial materials it is necessary to be on guard against unscrupulous vendors or manufacturers. They sometimes exercise a diabolical ingenuity in getting a good sample into the analyst's hands when perhaps the bulk of the material is indifferent or bad. Accurate sampling is difficult enough when we have to deal with the natural vagaries of raw materials, but the matter

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[1] E. H. Dickenson, *School Mines Quart.*, 35, 1, 1914.
[2] See W. L. Baillie, *Chem. Trade Journ.*, 56, 333, 1920; J. C. Munch and G. L. Bidwell, *Journ. Assoc. Off. Agric. Chem.*, 11, 220, 1928; L. Fresenius, *Metall Erz.*, 25, 395, 1928; A. E. R. Westerman, *Chem. Met. Eng.*, 36, 292, 1929; *Journ. Amer. Cer. Soc.*, 11, 264, 1928; F. P. Knight, junr., *ib.*, 15, 444, 1932; A. Baader, *Messtech.*, 11, 48, 1935; *British Eng. Stand. Assoc.*, Report 403, 1930; *British Stand. Inst.*, Specifications 496, 502, 1933.

is still more difficult when we are confronted with ingenious artifices meant to deceive. Faked samples soon accumulate in a laboratory, as inventors are fertile in resource and the field is always verdant.

The chance or probability of a sample answering expectations might be compared with the chance of drawing the ace of diamonds from a new pack of cards; of throwing a six with a dice, or of tossing "heads" with a penny. The probability of these events is very different, and the probability of obtaining a representative analysis for material in bulk from a grab sample depends upon the nature of the material. The less homogeneous the material the less likely is the grab sample to represent the character of the material in bulk (see size ratio, page 118). Samples selected by a vendor for advertising purposes are here excluded from consideration, because the chance of getting a "first-class result" can sometimes be compared with the probability of throwing a six with a dice loaded for that number.

§ 62. Selecting the Sample.

If the material be in slip—for instance, in checking the composition of a glaze in the dip tub—the material must obviously be thoroughly agitated before the sample is taken, or difficulties will arise owing to settling. A device like that indicated in fig. 43 is useful for withdrawing samples from different parts of a

Fig. 43.—Slip Sampler.

tub or an ark of slip. The end of the tube A with the plug B pulled tightly into its socket by means of the wire and handle C is sunk to the required depth in the slip. The plug is then pushed downwards for a few moments. Slip runs into the lower end of the tube. The plug is then pulled back into its socket, and the tube with the slip inside withdrawn. The slip can be removed in an obvious manner. Metzger[1] has a much more complicated device by which several samples may be taken simultaneously at several different depths.

The sample of slip must be dried and then thoroughly mixed. This arises from the fact that clay and glaze slips, on standing, are liable to separate into layers of different composition.

With powdered manufactured or natural products, grab samples can be selected from a number of different parts of the stuff in bulk. A cheese scoop
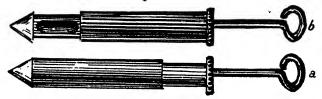
Fig. 44.—Metzger's Sampler.

is useful for drawing portions from stuff in bins or sacks. Metzger (*loc. cit.*) has devised a good sampler for this purpose (fig. 44).[2] In the diagram (*a*) it is

[1] P. Metzger, *Zeit. anal. Chem.*, 39, 791, 1900; O. Steinle, *Zeit. angew. Chem.*, 5, 584, 1892; A. Gawalovski, *Allgem. Österr. Chem. Tech. Ztg.*, 6, 197, 1889.
[2] R. Kroupa, *Berg. Hütt. Ztg.*, 48, 301, 1887; J. T. Stoddard, *Journ. Anal. App. Chem.*, 4, 34, 1890; J. W. Kellogg, *Journ. Ind. Eng. Chem.*, 14, 631, 1922.

represented ready for insertion.   When inserted it is screwed so that an opening is made for collecting the material to be sampled (*b*).   Another turn will close the apparatus ready for withdrawal (*a*).

The number and size of the different grab samples is determined by the nature and size of the material under investigation.   A ship-load of bone, for instance, wants different treatment from a truck-load of clay, a boat-load of felspar, or a load of borocalcite.

Accurate sampling can only be performed when the materials can be pulverised.   A perfect method of sampling must eliminate the personal factor and work with machine-like precision.   This is quite easy with powdered materials intimately mixed, and the "time-sampling machines" which grind and periodically select a fraction of the whole do this work very well.   This kind of sampling is seldom practicable in dealing with clays and potters' materials.[1]   In sampling many ores, 5 per cent., that is, one-twentieth of the whole, is supposed to be selected in portions of equal weight and at frequent intervals.   If the material is being delivered in shovels, every twentieth shovel is sometimes put on one side; if delivered in barrows, every twentieth barrow; if in sacks, every twentieth sack, and so on, according to the nature of the material to be sampled.   With cargoes of some materials "one-in-fifty" will be ample.

§ 63. Reducing the Bulk of the Sample.

A large sample must be reduced in bulk before it can be treated in the laboratory.   The reduction may be done by hand or machine.   There are at least five hand methods available for reducing the sample to a convenient bulk for treatment in the laboratory: (1) fractional selection; (2) quartering; (3) channelling; (4) split shovelling; and (5) riffling.   In machine sampling the material may be (1) divided into two or more unequal streams, and one or more streams reserved for the sample (split-stream samplers); (2) the whole of the stream may be taken off intermittently (time samplers).

(1) *Sampling by Fractional Selection.*—The selection of 5 per cent. of the total bulk of the material (heap A) to be sampled as indicated above is an illustration of this method of sampling.   The first sample (heap B) is ground, if necessary, into grains on average, say, one-twentieth the size of the first sample, and every twentieth shovel or barrow-load collected into another heap, C; this is again ground and subdivided until one or two hundredweights are obtained in a heap, say D.   The operations are summarised as follows:—

$$A = 1000 \text{ tons of a cargo of material to be sampled};$$
$$B = 50 \text{ tons in first fraction};$$
$$C = 2 \cdot 5 \text{ tons in second fraction};$$
$$D = 0 \cdot 125 \text{ ton or } 280 \text{ lbs. in the third fraction}.$$

Hence, if *w* represents the weight of material in the mass to be sampled, the *n*th fraction will have $w(0 \cdot 05)^n$th part of the original bulk.

(2) *Sampling by Coning or Quartering.*[2]—A homogeneous pile of the material is built up as a cone about a real or imaginary rod as centre.   Every shovelful

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[1] For the sampling of ceramic materials, see Report, *Journ. Amer. Cer. Soc.*, **5**; *Year Book 1921/22*, 36, 1922; H. Knuth, *Tonind. Ztg.*, **53**, 270, 1929; A. E. R. Westerman, *Bull. Amer. Cer. Soc.*, **15**, 168, 1932; G. A. Johnson, *ib.*, **15**, 170, 1932; F. F. Grout, *Amer. Journ. Sci.*, **24**, 394, 1932.

[2] W. Glenn, *Trans. Amer. Inst. Min. Eng.*, **20**, 155, 1890/91; C. M. Roberts, *ib.*, **28**, 413, 1898; P. Johnson, *Eng. Min. Journ.*, **53**, 111, 132, 1892; E. H. Smith, *ib.*, **95**, 579, 1913; F. White (*Min. Eng. World*, **38**, 1043, 1913) examines the accuracy of quartering by mixing ground ore with coloured beads and concludes that absolute accuracy is not obtainable.

of the material is thrown directly on top of the growing cone, so that it runs and spreads more or less evenly down the sides. As a matter of fact, the fine material has a tendency to accumulate about the centre of the cone, while the coarse material rolls down the sides and an almost imperceptible sorting occurs (see fig. 48). The operator, in building up the cone, drops the shovel of material on top of the cone by giving the shovel a jerk upwards (just over the apex of
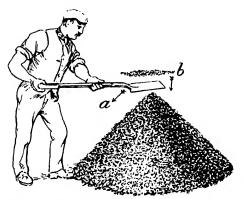
FIG. 45.—The Cone almost ready for Flattening.

the cone), and then another jerk downwards and outwards as indicated by the arrow a, fig. 45. The material falls downwards on the apex of the cone, b, fig. 45. With experienced men, the circumference of the cone, when finished, will be nearly circular. The cone is then spread out into a "pancake" by means of shovels working from the centre to the periphery round and round the cone
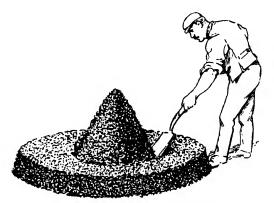
FIG. 46.—The Cone Partially Flattened.

(fig. 46). The pancake is then separated into quarters by means of boards or steel blades (fig. 47), pointing, say, north and south, and east and west. If the N.E. and S.W. quarters are rejected, the N.W. and S.E. quarters are piled into another cone, and again quartered. Thus 200 lbs. would be reduced by the first cut to 100 lbs. A second cut would reduce this to 50 lbs. And generally, starting with a weight w of material, the nth cut gives by quartering a weight $w(0.5)^n$th of the original weight w. Thus, starting with 200 lbs., the tenth cut will give $200 \times (0.5)^{10} = 0.195$ lb.

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Two men can reduce a ton of material down to a few pounds in two or three hours. Perfect mixing, accurate subdivision and thorough cleanliness are essential to success in all the methods for reduction.

It will be noticed that owing to the accumulation of the fine material towards the centre, if the apex of the cone be deliberately or accidentally deflected while being built, it is possible and probable that in levelling, the first layers, at the bottom of the cone, will lie wholly in one quarter, and thus the proportion of fine material in that quarter will be abnormally high. The effect of imperceptibly drawing the centre of the cone on the relative proportion of fine and coarse material will be evident from fig. 48 (after Brunton), which is a photograph of a cone built up in actual sampling practice, bisected by a sheet of glass, and one-half of the cone removed. The diagram shows well the structure of a cone with a drawn centre.[1]
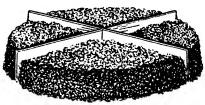
FIG. 47.—" Pancake " Cutting.
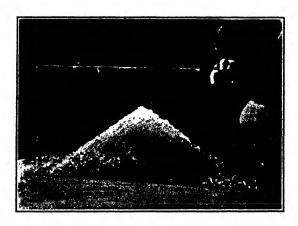
FIG. 48.—"Drawn" Cone. (After J. D. Brunton.)

(3) *Sampling by Channelling*.[2]—The material to be sampled is spread out in the form of a square about 4 inches thick. Parallel grooves—say 1 foot apart—are cut across the cake; and then another set of grooves at right angles to these. The process is repeated with the material so cut from the square. The method is slow and inaccurate, for coarse pieces may fall into the grooves as they are being cut.

(4) *Split-shovel Sampling*.—One workman (left, fig. 49) throws the material from a broad shovel upon a narrow U-shaped scoop-like shovel held by another workman (right, fig. 49) over a car or wheelbarrow (fig. 49). The material which remains on the shovel is retained. When a pile of this has accumulated it may be further reduced in bulk by repetitions of the process. There are

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[1] J. D. Brunton, *Trans. Amer. Inst. Min. Eng.*, 40, 675, 1909.

[2] F. A. Lowe, *Eng. Min. Journ.*, 31, 203, 1881; W. Glenn, *Trans. Amer. Inst. Min. Eng.*, 20, 115, 1890/91. For a mechanical device for cone-sampling, see C. W. Kneff, *Journ. Ind. Eng. Chem.*, 4, 682, 1912.

several different types of split shovel.[1] Some have a series of such scoops on one shovel, with spaces and scoops equal in width.

FIG. 49.—Sampling by the U-shovel or the Split Shovel.

(5) *Riffle Sampling.*— The riffle consists of a series of grids arranged to form alternate series of troughs and spaces. When the material to be sampled is spread by means of a shovel over the riffle, supported over, say, a wheelbarrow, part of the material passes into the barrow, and part remains in the troughs.

FIG. 50.—Taylor and Brunton's Split-stream Sampler.

When the troughs are full, the contents are put on one side for further trial. That which passes through the grids is rejected. There are several modifica-

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[1] J. D. Brunton, *Eng. Min. Journ.*, 51, 718, 1891; S. A. Reed, *School Min. Quart.*, 3, 253, 1882.

tions. In Jones' riffle the troughs are inclined, and slope in opposite directions. There are no spaces. The material when spread over the troughs (2 in. wide) is broken into two streams passing in opposite directions, and each stream is collected in a suitable receptacle. The riffle is usually employed for cutting down samples for the laboratory when the amount is too small for the larger mechanical samplers.

Taylor and Brunton's splitter (fig. 50) is a modification in which numerous small spouts are arranged across the entire width of a large gutter, so that the main stream of the material, poured into the gutter, is divided into a number of smaller streams. The odd-numbered streams may be deflected to, say, the right, the even-numbered streams to the left. The material which collects on one side is rejected; the other—the sample side—is retained. The method of pouring will be obvious from fig. 50. The operations are repeated on the material which has passed through the divider as often as desired.

These samplers reduce the volume 50 per cent. each time the material is treated, as is the case in quartering. It is important to mix the material collected on the sample side thoroughly before it is passed through again.[1]

§ 64. Machine and Automatic Sampling.

Split-stream Samplers.—In Clarkson's divider,[2] the material is poured into a funnel where it is split into six similar streams (fig. 51). The material

Fig. 51.—Clarkson's Split-stream Sampler.

before it is placed in the funnel is supposed to have been ground to pass at least an 8's lawn. It is fundamentally important in all systems of sampling to make sure that the "sample" and "reject" are of the same composition.

There are many other types on the same principle. In some, a series of funnels are superposed one above the other, so that a fraction of the stream is

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[1] J. D. Brunton, *Trans. Amer. Inst. Min. Eng.*, **40**, 567, 1909.
[2] T. Clarkson, *Journ. Soc. Chem. Ind.*, **12**, 214, 1894.

rejected and another fraction is further fractioned as it passes on to the sub-jacent funnel, *e.g.* F. W. Braun's "Umpire" sampler,[1] which is excellent.

Time Samplers.—In the time-sampling machine, the whole of a falling stream of the material is periodically deflected during a portion of the time. This eliminates one fault with split-stream samplers—where the sizes of the grains are never evenly distributed across the stream. In some, on a large scale, the material is alternately subdivided and crushed from the coarsest down
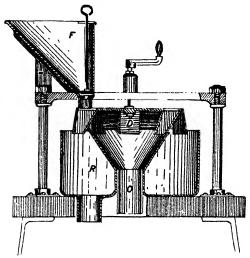
FIG. 52.—Bridgman's Time Sampler.

to the finest powder. The machines are represented by Snyder's time sampler;[2] the Vezin time sampler;[3] and the Brunton time sampler. H. L. Bridgman's time-sampling machine[4] is a compact little instrument occupying but 14 square inches. It has a divider D set in motion by clockwork or any other power (fig. 52). F is a funnel with a receptacle R for the fraction separated from the material being sampled. The portion rejected passes through the discharge orifice O. The material runs from the hopper in a continuous stream to the divider, which cuts the stream eight times during one revolution. Four of these cuttings are delivered into the discharge orifice, and four are delivered into the receptacle.

§ 65. Reducing the Grain Size and Bulk of the Material during Sampling.

The process of sampling involves two operations: (*a*) reducing the bulk of the material as indicated in the preceding sections; (*b*) reducing the size of the grains of the material. The important factors in accurate sampling are: (1) the relation between the amount of material selected as the sample and the

[1] F. W. Braun, *U.S. Pat. No.* 682528, 1901.
[2] F. T. Snyder, *Canada Min. Rev.*, 17, 43, 1898.
[3] H. A. Vezin, *Trans. Amer. Inst. Min. Eng.*, 26, 1098, 1896.
[4] H. L. Bridgman, *Trans. Amer. Inst. Min. Eng.*, 13, 639, 1884; 20, 416, 1890/91; *U.S. Pat. No.* 553508, 1896. For other types of samplers, see J. G. King and D. MacDougall, *Fuel*, 12, 93, 1933; A. Dawe and N. M. Potter, *ib.*, 12, 313, 1933; W. L. Baillie, *Chem. Trade Journ.*, 56, 335, 1920.

original bulk of the material to be sampled—the bulk ratio; (2) the relation between the coarseness of the grain and the amount—the size ratio (sampling); (3) the relation between the size of the grain and the amount isolated at each stage of quartering, etc.—size ratio (quartering).

(1) *The Relation between the Bulk of the Sample and of the Material to be Sampled.*—The greater the ratio between the weight of the sample and the weight of the whole of the material sampled, that is, the greater the ratio,

$$\frac{\text{Weight of sample}}{\text{Weight of material in bulk}} = \text{Bulk ratio}$$

the greater the probability of the sample representing the true character of the material under investigation. This is illustrated by the following table, due to Bailey :—

Table XVI.—Relation between Errors in Sampling and Size of Sample.

Bulk ratio.	Percentage error—sample and bulk.
1 : 100	1·4
2 : 100	0·8
5 : 100	0·6

(2) *The Relation between the Grain Size and the Weight of the Sample.*—The smaller the ratio between the weight of the largest pieces and the total weight of the sample, that is, the smaller the fraction,

$$\frac{\text{Weight of largest pieces in sample}}{\text{Total weight of sample}} = \text{Size ratio}$$

the more likely is the sample to represent the character of the material in bulk. Bailey's experiments [1] on sampling coal (with 5 per cent. ash) illustrate this point very well. He found that if the maximum error is to be less than 1 per cent., with a probable error of nearly 0·2 per cent., the relation between the total weight of coal taken and the weight of the largest pieces in the coal must be near that indicated in the following table:—

Table XVII.—Relation between Largest Pieces and Total Weight of Sample.

Weight of largest pieces in lbs.	Amount of sample not less than (lbs.).
6·7	39,000
2·5	12,500
0·75	3,800
0·38	1,900
0·24	1,200
0·12	600
0·046	230
0·018	90

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[1] E. G. Bailey, *Journ. Ind. Eng. Chem.*, **1**, 161, 1909; **2**, 543, 1910; F. C. Weld, *ib.*, **2**, 426, 1910; F. Fischer, *Stahl Eisen*, **32**, 1408, 1912; W. B. Blyth, *Min. Eng. World*, **37**, 613, 1912.

Under these conditions the sample is less likely to be disturbed by an accumulation of abnormally fine dust or coarse material.

(3) *The Grain Size of each Fraction (Quartering).*—The relation between the grain size and the amount to be isolated at each stage of the quartering is an important factor, as will be obvious from the preceding notes on the relation between the grain size and the amount to be selected as a sample. Continuing the experiments just described, Bailey found that in order to get the deviations in the composition of the ash of coal within the limits stated, it was necessary to reduce the sample before quartering or fractioning to the grain size indicated in the following table:—

Table XVIII.—Relation between Fineness of Sample and Bulk of Material.

Weight of fraction in lbs.	Size when crushed. Diam. in inches.
7500	2
3800	1·5
1200	1
460	0·75
180	0·5
40	0·425 (2's mesh)
5	0·20 (4's mesh)
0·5	0·1 (8's mesh)
0·25	0·076 (10's mesh)

According to Bailey, if the laboratory sample be crushed to pass a 2's mesh, a fraction of not less than 8300 grms. should be collected without further grinding; for a 4's mesh, not less than 1100 grms., etc., as indicated below:—

Size of mesh	2	4	8	10	20's
Minimum amount	8300	1100	120	55	3 grms.

Naturally the best value for the bulk and size ratios defined above will vary with the nature of the material and the degree of accuracy demanded in the sampling. In the absence of data for particular materials, the preceding data will serve as a guide in determining these factors.[1]

To summarise, good sampling involves: (1) Adequate mixing; (2) Impartial selection; (3) Proper grinding.

There is always a danger in applying rules blindly. The exercise of common sense, guided by these three principles, is necessary to cope with the different problems which arise from time to time. All the preceding discussion would

[1] For papers on the theory of sampling see P. Argall, *Trans. Amer. Inst. Min. Eng.*, **31**, 235, 1901; D. W. Brunton, *ib.*, **25**, 826, 1895; S. H. Pearce, *Chem. Met. Soc. S.A.*, **2**, 155, 1898; S. A. Reed, *School Min. Quart.*, **3**, 253, 1882; **6**, 351, 1885; A. D. Hodges, *Eng. Min. Journ.*, **52**, 264, 1891; V. Samter, *Chem. Ztg.*, **32**, 1209, 1224, 1250, 1908; C. Geissler, *ib.*, **23**, 43, 1058, 1899; E. Jensch, *ib.*, **18**, 70, 1894; L. Rump, *ib.*, **18**, 32, 1894; *German Pat. No. D.R.P.* 100067, 1898; 100516, 1898; O. Bender, *Zeit. anal. Chem.*, **48**, 32, 1909; *Zeit. Berg. Hütt. Sal.*, **55**, 1, 1907; F. Janda, *Oester. Zeit. Berg. Hütt.*, **52**, 547, 561, 577, 1904; J. A. Barral and R. Duval, *Dingler's Journ.*, **217**, 246, 1876; M. L. Griffin, *Journ. Soc. Chem. Ind.*, **24**, 183, 1905; W. Glenn, *ib.*, **17**, 123, 1898; C. E. Stromeyer, *Pract. Eng.*, **44**, 781, 1911; L. T. Wright, *Chem. Eng.*, **13**, 30, 1911; A. C. Fieldner, *ib.*, **17**, 50, 1913; M. Webber, *Min. Scientific Press*, **107**, 846, 1911; *ib.*, **113**, 846, 1917; C. S. Haley, *ib.*, **111**, 79, 1915; Report, *Zeit. angew. Chem.*, **26**, 513, 1913; *Ann. Chim. anal.*, **19**, 186, 1914; *Journ. Chem. Techn.*, **2**, 17, 1914; Report, *Drugs, Oils, Paints*, **31**, 47, 1915; Report, *Amer. Soc. Testing Materials*, 544, 554, 1916; M. C. Holmes, *Journ. Franklin Inst.*, **219**, 483, 1935; *Ind. Eng. Chem. Anal. Ed.*, **7**, 112, 1935.

be misleading if the object of the investigation were to determine the composition of a specific mineral. In that case the purpose would probably be best served by very carefully isolating as clean and as pure a crystalline fragment as possible. All associated impurities, foreign matter and all altered fragments should be excluded. Neglect of this precaution would render it necessary to admit the existence of innumerable varieties of a particular mineral, but even with the best of precautions, ideal conditions cannot be attained. An examination of thin slices under a microscope shows how very seldom a pure mineral can be obtained free from foreign inclusions, *e.g.* quartz crystals may enclose rutile, pyrites, chlorite; leucite often some augite; staurolite, some cyanite and quartz; analcime, some apophyllite.[1]

§ 66. Sampling Beds of Clay.

Another type of sampling is sometimes required. To find if it is advisable to install plant for working a natural bed of clay, it is necessary to make a somewhat close approximation to the amount of clay available, as well as to determine the nature of the clay, possible market, cost of transport, fuel and labour. Here we are alone concerned with making an estimate of the amount of clay and the collection of samples for investigation.

In sampling an unworked bed of clay near the surface, a hole may be sunk through the different strata well into or through the clay under investigation, and 28-lb. grab samples taken from the exposed face. It is well to keep for reference small samples of the different superincumbent strata. Care must be taken in digging and sampling the hole not to mix fragments from one stratum with those of another. The distance between the original locus of the different samples and the surface should be measured and recorded on and in the boxes or bags in which the different samples are preserved. If the clay under investigation is any great distance from the surface, this procedure would be laborious if the thickness and extent of the clay had to be explored. Many of the well-known types of borer bring a core to the surface with much less labour than is involved in digging holes, as described above. The type of borer to be used is largely determined by the hardness of the different strata and the depth of the required boring. Two men can conveniently work one of H. Meyer's borers to a depth of 30–50 feet in a few hours.[2] Fraenkel's borers can be sunk about 12 feet by one man in a few hours in ordinary surface clays. Bore-holes have been driven by power over 7350 feet.[3] The cost for the deep-seated clays would generally be prohibitive, although bores ranging up to 500 feet are common enough. When a series of cores properly measured has been obtained, the nature of the clay can be investigated by methods to be described later.

Much naturally depends on the geological character of the bed in question. The continuity, thickness and nature of a bed of fireclay in, say, the coal measures in a given area can often be predicted with a high degree of probability by a geologist provided with particulars of the same stratum in part of the prescribed area. Hence a boring within the prescribed area can only

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[1] C. Rammelsberg, *Zeit. anorg. Chem.*, **1**, 335, 1892; S. L. Penfield, *Amer. Journ. Sci.*, (4), **10**, 19, 1900.

[2] A. Fauck, *Anleitung zum Gebrauche des Erdbohrers*, Leipzig, 1877; *Suppl.*, 1899; H. Bansen, *Das Tiefbohrwesen*, Berlin, 1912.

[3] With rotary diamond drills—2003·34 metres at Paruschowitz (Upper Silesia)—*B.A. Rep.*, 67, 1901; with percussion drills—5570 feet at Sperenberg (about 25 miles south of Berlin)—H. W. Bristow, *Geol. Mag.*, **4**, 95, 1875; B. Jäger, *Zeit. Berg. Hütt. Sal.*, **59**, 89, 1911.

demonstrate what was almost a certainty.[1] A skilled geologist may be able to correlate the stratum under investigation with another known stratum elsewhere. The nature of certain strata frequently persists throughout wide areas; for instance, the peacock marl (N. Staffs.), the Old Mine clay (Stourbridge), Oxford clay and London clay. Other strata, and even the clays just mentioned, may vary in an apparently erratic manner in certain localities. A prudent man, therefore, will try to estimate what amount and what quality of clay is available.

Sampling and boring is somewhat costly work, but, when properly done, it gives a clear idea of the extent and nature of a hidden bed of clay, and it prevents awkward mistakes, such as the erection of the kilns and machine shed over what might be the best part of the clay.[2] Exposures and cuttings in a given neighbourhood may give enough information as to the amount of clay available in a given area without any need for an elaborate system of boring.

When a series of borings has been obtained, they may be recorded as follows. For convenience we apply the method to a particular problem. A few years ago, a valuable plastic clay 15 feet thick gave signs of tapering off.
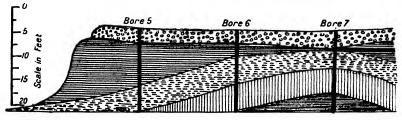
FIG. 53.—Section constructed from Borings.

A series of borings 20 feet deep was made, and it was proved that the clay seam "petered out" between 40 and 50 feet away from the working face. A new seam of a somewhat similar plastic clay was "struck" below a seam of a sandy clay. In boring systematically to find the extent of the new seam, what appeared to be the old seam was taken up not far from where it had tapered off. In boring, the "field" was divided into a series of imaginary rectangles resembling a chess-board. A boring was made at every corner. With the data so obtained diagrams were drawn to scale representing sections through the different strata in particular directions. One such section is illustrated in fig. 53. This is drawn from the borings Nos. 5, 6, 7, 8, which were:—

	No. 5.	No. 6.	No. 7.	No. 8.
	ft. in.	ft. in.	ft. in.	ft. in.
Overburden . .	2 8	2 10	3 0	2 5
Plastic clay . .	9 7	2 11	0 2	6 0
Sandy clay . .	7 8+	6 0	4 8	4 5
Plastic clay B. .	..	7 10+	5 0	6 2
Sand . . .	..	..	6 0+	3 2+

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[1] The process of boring may then be compared with interpolation in mathematics. The possibility of faults or folding may render an extrapolation futile and stultify a prediction.

[2] An instructive example occurs at an abandoned clay pit near Cobridge, Stoke-on-Trent.

The distance apart and depth of the borings for each particular "field" must be determined by the circumstances of the case and the advice of a geological expert may be needed.

§ 67. The Commercial Value of Clay Deposits.

In order to evaluate a clay deposit, it is necessary first of all to determine the commercial value of the goods to be made from the clay which, after all, reduces to the present market value of a cubic foot of the clay. Due consideration is of course paid to the district, facilities for transport, cost of fuel, etc. In some inaccessible districts land covering a first-class clay might have no more value than ordinary agricultural land, owing to lack of facilities for transport and cost of fuel. In the second place, it is necessary to determine how much clay is available. In the third place, an approximate estimate must be made of the yearly consumption of the clay, and consequently also how many years the seam of clay will last at the estimated rate of consumption. We are then in a position to deal with the problem by arithmetic.[1]

Let R represent the estimated value of the clay consumed per annum; r, the rate of compound interest for the money were it invested at the current rate; and n, the estimated number of years the clay is likely to last before the seam, or a given portion of the seam, is exhausted. The regular rules for compound interest show that the present value, P, of the given field of clay can be represented by the expression:

$$P = R\frac{p^n - 1}{p^n(p - 1)} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where, for convenience, we have written

$$p = \frac{100 + r}{100} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

To illustrate by example, suppose that 10,000 cubic feet of clay be removed each year; that 1,000,000 cubic feet of clay are still available.[2] The clay is worth $\frac{1}{4}$d. per cubic foot. The rate of interest is $3\frac{1}{2}$ per cent. What is the present value of the field of clay? Here $r = 3.5$; hence, from (2), $p = 1.035$. The 1,000,000 cubic feet of clay will last 100 years if 10,000 cubic feet be removed per annum. Also, $R = 10,000 \times \frac{1}{4} = 2500$d. Consequently, from (1),

$$P = 2500\frac{(1.035^{100} - 1)}{1.035^{100}(1.035 - 1)} = \text{£288, 1s.}[3]$$

It is then possible to decide whether it is better to pay an annual royalty for the clay, to pay a proposed rental, or to purchase the field at a stated price.

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[1] E. Tschenschmer, *Tonind. Ztg.*, 14, 121, 139, 1890; *Brit. Clayworker*, 18, 279, 1910; A. J. Huac, *Brick*, 49, 499, 1916.

[2] The estimation of the cubic contents of a given seam is simple arithmetic—solid mensuration—when the borings are known.

[3] Log $p^n = n \log p$.   Hence   100 log 1.035 = 100 × 0.0149333 = 1.49333 = log 31.141, or $1.035^{100} = 31.141$.

CHAPTER IX.

THE REAGENTS.

§ 68. Testing the Reagents.

THE purity of the reagents and of the distilled water for analytical laboratories should not be taken on trust.[1] The glass containers may contaminate liquid reagents with iron, potassium, sodium, silica, calcium and alumina by the dissolution of the glass; and zinc may be derived similarly from Jena glass vessels. Iron is common in acids transported in carboys. Small flakes of iron may scale from the blowpipes used by the glass-blower, and this may not be removed or noticed in washing these vessels. Reagents may be contaminated from their contact with the vessels—tanks, stills, condensers, crystallising dishes, etc., made from lead, silver, copper, iron, aluminium, nickel, zinc, tin, porcelain, glass, etc.—used in the process of manufacture. Thus, not only may the ordinary constituents of glass be present, but nickel may be found in caustic alkalies, copper and aluminium in acetic acid, zinc in barium carbonate,[2] selenium and iron in hydrochloric acid,[3] and lead in organic acids and in hydrofluoric acid. The latter has also been known to contain potassium sulphate and ammonium and sodium chlorides. Impurities may also be derived from the raw materials used in the process of manufacture.[4] In fact, it is almost impossible to free some reagents from certain impurities except at a very high cost. For example, iron, alumina and silica are found in all but the highest-priced grades of caustic alkalies and alkali carbonates; calcium is very difficult to remove from ammonium oxalate; sodium from calcium carbonate; nickel from cobalt; iron and lead from copper; free acid from ferric salts; and ammonia from magnesium chloride.[5] All this is mentioned to emphasise the fact that *constant vigilance is the price of successful work.* Many impurities might easily escape detection. For instance, selenium in hydrochloric acid; sulphates in platinum chloride; lead in ammonia; phosphorus in ammonium chloride and nitrate; and calcium in ammonium oxalate.[6] Hence, in quantitative

[1] The "analysed" chemicals supplied by many of the better-class makers are generally very good. C. N. Myers, *U.S. Public Health Rep.*, **31**, 2754, 1916; B. S. Drake, *Journ. Ind. Eng. Chem.*, **9**, 109, 1917; W. D. Collins *et al.*, *Journ. Soc. Chem. Ind.*, **44**, B695, 1925; *Ind. Eng. Chem.*, **17**, 756, 1925; **19**, 645, 1369, 1927; **20**, 979, 1928; *ib.*, *Anal. Ed.*, **1**, 171, 1929; **3**, 221, 1931; **4**, 347, 1932; **5**, 289, 1933.

[2] R. Wegscheider, *Zeit. anal. Chem.*, **29**, 20, 1890.

[3] W. B. Hart, *Chem. News*, **48**, 193, 1883.

[4] J. R. Withrow, *Journ. Ind. Eng. Chem.*, **9**, 771, 1917—sodium nitrate in nitric acid.

[5] J. W. Shade, *Journ. Amer. Chem. Soc.*, **28**, 1422, 1906; J. T. Baker, *Journ. Ind. Eng. Chem.*, **1**, 464, 1909.
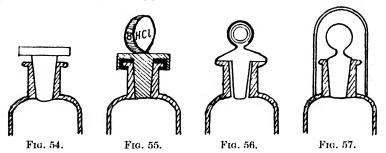
[6] C. Krauch gives the regulation tests for impurities in reagents in his *Die Prüfung der chemischen Reagentien auf Reinheit*, Berlin, 1896 (J. A. Williamson and L. W. Dupré's translation, New York, 1902); E. Merck, *Prüfung der chemischen Reagenzien auf Reinheit*, Darmstadt, 1912; or '*Analar*' *Standards*, London, 1934; J. Rosin, *Reagent Chemicals and Standards*, London, 1937.

analysis particularly, the reagents are best tested by blank analyses.[1] The blank analysis does not necessarily give absolute certainty, because the reactions without the substance are not necessarily the same as with the substance. In most cases, however, the blank analysis is an excellent and reliable method of testing the purity of reagents, and it frequently gives a means of correcting the results of the analysis proper.

The branding of reagents as "chemically pure"[2] is not a sufficient guarantee that the reagents are really pure enough for a particular purpose. Some reagents have been advertised as "absolutely C.P."; every chemist knows that it is practically impossible to make absolutely pure reagents in any quantity. The so-called "analysed reagents" are probably more reliable: it is certainly more honest to admit that we cannot get absolutely pure reagents, and that the next best thing is to know what and how much impurity is present. It is a question if the analysis shown on the label is always an absolute guarantee of the quality of the contents. Thus Lehner[3] quotes the label "Copper metal, sheet. Analysis: Fe, 0·001 per cent.; Sn, none; Sb, none; Cu, none." *Qui nimium probat, nihil probat.* The U.S.A. Bureau of Standards writes (31st March 1914): "We never take at their face value the statements on the labels, and often find them absolutely false. Others have had the same experience. This holds for foreign as well as domestic make."

§ 69. Bottles for Reagents.

In a laboratory where a number of workers use the same bottles, particular care must be exercised. Errors might easily creep into the work from an interchange of stoppers, placing stoppers on the working benches, mistakes in filling

FIG. 54.   FIG. 55.   FIG. 56.   FIG. 57.

and weighing out the reagents. The necks and mouths of all the bottles should be kept clean. The bottles and the stoppers should be numbered so that no confusion is possible. The "mushroom" stopper (fig. 54) is not sufficient to protect the mouth and lip of the bottle from dust and when these flat stoppers are stuck they are unusually difficult to loosen.[4] F. F. Jewitt has designed a

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[1] W. A. Dixon, *Chem. News*, 55, 228, 1887; *ib.*, 78, 294, 1898; G. Surr, *Min. Eng. Journ.*, 41, 1167, 1914.

[2] L. F. Kebler, *Journ. Franklin Inst.*, 153, 53, 1902.

[3] V. Lehner, *Journ. Ind. Eng. Chem.*, 6, 603, 1914.

[4] LOOSENING FIXED GLASS STOPPERS AND STOPCOCKS.—Usually the stoppers are not ground to fit the bottles well enough to prevent the slow evaporation of volatile liquids like ether or chloroform. The better the stopper is ground into the bottle, the more it is liable to stick. When a stopper is fixed, it can sometimes be loosened by tapping with the handle of a pocket-knife, followed by a twisting wrench with the fingers or a pair of pliers with a cloth between the pliers and the glass. Fixing the stopper, padded with a cloth, in the jaws of a vice and then twisting the barrel of the bottle is frequently effective. Too powerful a wrench will break the stopper. If the bottle still resists, warm the neck with a cloth wet with hot

stopper with a pendent flange (fig. 55), with the idea of protecting the mouth and lip of the bottle from dust. These stoppers are also very difficult to loosen when stuck. Swarts[1] has designed a glass stopper (fig. 56) which has the advantage of not sticking with solutions of caustic alkali. The cone of the stopper fits the neck of the bottle loosely, but the flat part of the stopper on the under side, as well as the corresponding neck of the bottle, are polished flat, so that a close joint is obtained.

We prefer to keep the regular reagents in 250- and 500-c.c. resistance or Jena glass bottles with stoppers shaped as indicated in fig. 57, and with a rubber or loose glass cap placed over the neck. When the bottles are in use, the stoppers can either be placed on a watch-glass or similar surface, or held between the fingers.

The acid bottles are best kept, if convenient, on sheets of glass or rubber which rest on wooden shelves.[2] The names on the acid bottles should be sand-blasted or enamelled. For other bottles the proper designation should be written in Indian ink on a gummed label. When the ink is dry, the label is gummed to the bottle and then coated with size. When the size is dry, the whole is varnished [3]—one or two coats. Solids and liquids are usually supplied in corked or stoppered bottles. Their labels should be sized and varnished, as indicated above, before the bottles are shelved. Otherwise a bottle may be found with a label missing at an inconvenient time. Unprotected labels have a way of dropping off, and the writing is liable to fade in humid climates.

When an analysis—qualitative or quantitative—is in progress, the beakers, basins, flasks and funnels should be labelled without delay. This will prevent confusing filtrates, precipitates and samples with one another. A circular or oval patch can be sand-blasted on the various pieces of glass apparatus so that they can be marked with a lead pencil, or a special pencil for writing directly on glass or porcelain can be used. Such pencils write best if the surface is clean and warm.

water, or, better, slowly warm the bottle by turning the neck rapidly in a Bunsen's flame at intervals of about a minute. The temperature of the neck is thus slowly raised. The stopper can be given a tap and wrench immediately after the neck has passed through the flame. Too great or too sudden heating will fracture the bottle. An obstinate stopper can sometimes be removed by leaving a little oil or glycerine above round the neck of the bottle, say overnight. A tap and wrench may then loosen the stopper. If the stopper be still fast, invert the bottle in a vessel of water so that the water reaches to the shoulder of the bottle. Let the bottle be inclined so as to prevent a bubble of air being entrapped in the gutter between the stopper and the bottle. This would prevent the water gradually working its way between the stopper and the bottle. The stopper may be tried with the tap and wrench after standing one, two, three, or four days. If it still resists, warm the water. As the water is warming, the bottle may be removed every now and again, to find if the stopper will yield to the tap and wrench. Time and patience are generally effective. Sometimes the bottle is wanted at once, and the tapping and wrench, or the heating over the Bunsen burner, are continued until either the stopper loosens or the bottle breaks. The means taken to prevent accidents will naturally depend on the contents of the bottle. The naked flame would not be tried with a bottle of ether, nor would such a bottle be heated very much. See also H. W. Bailey, *Ind. Eng. Chem. Anal. Ed.*, **4**, 324, 1932.

[1] T. Swarts, *Chem. Ztg.*, **14**, 836, 1890; A. Gawalovski, *Rundshau*, 1131, 1890; *Oel-Fett-Industrie*, **9**, 114, 1892.

[2] Painting the side of the lip of the bottle—not the top of the bottle—with melted paraffin prevents solutions trickling down the outside, and incidentally facilitates the delivery of the reagent in drops. *Chem. News*, **65**, 179, 1892.

[3] PAPER VARNISH.—Quick-drying "paper" or "copal" varnish, from dealers in artists' materials, gives good results—the copal varnish for preference. If the size or varnish be unsuitable, or if the label has been imperfectly sized, unsightly greasy-looking patches will appear on the label. The first coat of varnish must be "set hard" before the second is applied.

§ 70. The Action of Reagents on Glass and Porcelain.

In his study of the alleged transformation of water into earth, Lavoisier [1] (1770) showed that water dissolves glass vessels. This subject is of great importance in analytical chemistry. Errors may arise owing to the action of the acid on the glaze of the porcelain basins during the silica evaporation, and some glazes are more readily attacked than others. Even the best of dishes are much eroded after they have been in use some time. Some of the poorer types of porcelain may lose 0·005 grm. in weight after a four-hours'evaporation of the hydrochloric acid solution, while the better types will not lose 0·0005 grm. by a similar treatment. The former number means that in a clay analysis with *two* evaporations, in that type of porcelain, the silica precipitate may be augmented 0·006 grm., the alumina precipitate 0·002 grm., and the lime precipitate 0·0003 grm. This matter therefore requires some attention. The difficulty is overcome by evaporating in platinum basins, but the high cost of platinum makes it necessary in ordinary circumstances to use porcelain glazed with a resistant glaze.

The action of different solutions on glass is far more vigorous than on porcelain, but some types of glass resist better than porcelain with an unsuitable glaze. It is therefore bad, on principle, to allow filtrates to lie any length of time in porcelain or glass vessels—particularly the latter. In some cases the contamination from the glass may be serious. Thus, if glass contains arsenic [2] (page 285), an error may arise in toxicological work with serious consequences. A great many investigations have been made on the action of water and various solutions on glass and porcelain vessels.[3] The following may be taken to represent the amount in milligrams dissolved by 100 c.c. of the given reagents in four hours:—

Table XIX.—Action of Reagents on Porcelain and Glass.

	Water.	HCl (20 per cent.).	H_2SO_4 (24 per cent.).	KOH (1 per cent.).	Na_2CO_3 (6 per cent.).
Berlin porcelain evap. basin	0	0·06	0	5·6	3·3
German porcelain evap. basin	1·8	0·4	0·6	1·1	9·2
Bohemian glass flask	1·8	0·1	0·6	1·2	1·75
Common glass flask .	1·4	2·7	8·0	5·3	4·8

[1] A. L. Lavoisier, *Œuvres*, Paris, **2**, 1, 1864.

[2] W. Fresenius, *Zeit. anal. Chem.*, **22**, 397, 1883; S. R. Scholes, *Journ. Ind. Eng. Chem.*, **4**, 16, 1912.

[3] R. Fresenius, *Anleitung zur quantitativen chemischen Analyse*, Braunschweig, **2**, 767, 1905; Eng. translation, London, **2**, 626, 1900; A. Emmerling, *Liebig's Ann.*, **150**, 257, 1869; R. Weber and E. Sauer, *Zeit. angew. Chem.*, **4**, 662, 1891; *Ber.*, **25**, 70, 1814, 1892; F. Kohlrausch, *ib.*, **26**, 2998, 1893; F. Foerster, *ib.*, **25**, 2494, 1892; **26**, 2915, 1893; F. Mylius and F. Foerster, *ib.*, **22**, 1092, 1889; **24**, 1482, 1891; *Zeit. anal. Chem.*, **31**, 141, 1892; F. Foerster, *ib.*, **33**, 299, 322, 1894; C. Bunge, *ib.*, **52**, 15, 1913; P. Truchot, *Compt. rend.*, **78**, 1022, 1874; R. Cowper, *Journ. Chem. Soc.*, **41**, 254, 1882; W. A. Hamor, *Amer. Druggist*, **62**, 29, 1914; *Journ. Ind. Eng. Chem.*, **6**, 508, 1914; W. D. Collins and H. B. Riffenburg, *ib.*, **15**, 48, 1923; E. Pfeifer, *Wied. Ann.*, **44**, 239, 1835–39; P. Nicolardot, *Chim. et Ind.*, **9**, 233, 469, 1923; *Compt. rend.*, **163**, 355, 1916; R. von Walther, *Journ. prakt. Chem.*, (2), **91**, 332, 1915; C. J. van Nieuwenburg, *Chem. Weekb.*, **14**, 1034, 1917; C. E. Klamer, *ib.*, **22**, 140, 1925; R. Dubrisay, *Bull. Soc. chim.*, (4), **27**, 409, 1920; W. E. S. Turner and T. E. Wilson, *Journ. Soc. Glass Tech.*, **6**, 17, 1922; W. E. S. Turner, *ib.*, **6**, 30, 1922; W. Meyer, *Chem. Ztg.*, **52**, 151, 1928; L. Springer, *Sprechsaal*, **62**, 187, 206, 1929; *Chem.*

From Cowper's work it appears that solutions of ammonium chloride and of ammonium sulphide usually attack glass rather more vigorously than sodium carbonate. It is important to bear these facts in mind when precipitations are made in ammonium sulphide solutions and left for some time, as is often done, to ensure the complete precipitation of the sulphides.

Mylius and Foerster give the following data for the action of water, $2N$-NaOH and N-H_2SO_4 solutions at $100°$ for six hours, and a $2N$-Na_2CO_3 solution at $100°$ for three hours. The numbers represent milligrams per square decimetre.

Table XX.—*Action of Reagents on the Best Types of Glass Apparatus.*

Type of Glass.	Beakers.					Flasks.				
	Water.		H_2SO_4.	NaOH.	Na_2CO_3.	Water.		H_2SO_4.	NaOH.	Na_2CO_3.
	$20°$.	$80°$.				$20°$.	$80°$.			
"R"	0·0054	0·0144	0	41	23	0·0128	0·0128	0	51	26
Jena	0·0071	0·0035	0	53	19	0·0063	0·0057	0	63	24
Bohemian	0·118	0·219	5	37	49	0·093	0·255	11	52	70

We are thus in a position to form some idea of what is taking place when filtrates are allowed to stand any length of time in porcelain or glass vessels. To illustrate the possible constituents to be found in the product of the reaction between the reagents and different types of glass, the following analyses are quoted from Walker's investigation[1] on chemical glassware:—

Table XXI.— *Composition of Chemical Glassware.*

Trade Name.	SiO_2.	Al_2O_3 and Fe_2O_3.	MnO.	ZnO.	MgO.	CaO.	K_2O.	Na_2O.	B_2O_3.	As_2O_3.
J. Kavalier's Bohemian	76·02	0·64	tr.	..	0·30	7·38	7·70	7·60	..	..
Resistance "R"	68·00	2·32	0·14	2·40	5·04	4·80	1·82	10·17	5·53	0·24
"Wiener Normal Geräthe Glas."	74·00	0·66	0·01	0·24	0·16	7·76	5·51	9·69	2·15	..
Thüringen.	74·36	0·90	tr.	..	0·16	9·40	0·14	14·83	..	..
"Schott & Gen., Jena"	66·74	2·77	0·65	8·28	4·50	0·28	0·08	8·99	7·18	..
"Nonsol W.T. Co."	65·04	3·78	0·04	8·88	1·44	1·75	0·08	12·72	6·23	..
Bohemian	70·80	1·00	1·04	..	0·08	7·88	7·67	8·59	..	..

The glaze of porcelain basins contains silica, alumina, alkalies and alkaline earths. The glaze is of a felspathic type, with or without lime. In work with silicates, therefore, it is unfortunate that the impurities introduced from the

Zentr., (1), 3027, 1929; S. Moriyasu, *Journ. Soc. Chem. Ind. Japan*, **34**, 314 B, 358 B, 1931; O. G. Burch, *Bull. Amer. Cer. Soc.*, **13**, 200, 1934; *Glass*, **11**, 348, 1934. For a lengthy discussion on this subject, see H. Hovestadt, *Jena Glass*, London, 319, 1902. For toughened glass, see R. J. Friswell, *Chem. News*, **52**, 5, 1885; J. S. Stas, *ib.*, **17**, 1, 1868; F. Siemens, *Journ. Soc. Arts*, **33**, 386, 1885.

[1] P. H. Walker, *Journ. Amer. Chem. Soc.*, **27**, 865, 1905; P. H. Walker and F. W. Smither, *Journ. Ind. Eng. Chem.*, **9**, 1090, 1917.

glass and porcelain vessels are those very constituents which have to be specially determined.

A few rules may now be indicated:—(1) If possible, do not allow the solutions to stand in glass or porcelain vessels for any length of time, particularly in glass. (2) If the work be interrupted, so that solutions must stand over, if there be no other objections, acidify the alkaline solutions before they are placed on one side. (3) If solutions must stand over, it is better to use good porcelain than glass vessels. (4) A resisting glass should be used for general work in place of the more soluble types of glass. (5) For exact work, a blank experiment should be made, using nothing but the regulation reagents, in similar quantities, and under similar conditions to those actually used in the analysis proper. This plan not only corrects for impurities in the reagents, but it also enables us practically to eliminate the sources of error now under discussion. This has been done in the examples given on page 168. (6) Precipitations made in alkaline solutions which have stood some time in glass vessels are almost certain to be contaminated with silica, and in exact work a correction must be made—e.g. cobalt and nickel precipitations, page 418. (7) Remember that solutions of reagents are usually kept in glass vessels. Such solutions may accordingly be contaminated with silica, etc. See, for instance, the determination of phosphorus by the colorimetric process, page 682.[1]

§ 71. The Equivalent System of Making Solutions.

There are many advantages in making the concentrations of the solutions used in analytical work follow a definite system. Some analysts make the solutions, as nearly as possible, on the "1, 2, 5, 10, 20, . . . parts of reagent per 100 parts of water" system. Wollny[2] recommends using multiples or submultiples of the equivalent weight (page 36) used in volumetric analysis, but the solutions need not be made up with such a degree of accuracy as obtains in volumetric analysis. Hence, the amount of reagent in a given volume of solution is approximately known, and equal volumes of the reagents bear a fixed relation one to another. For instance, an "E" solution of barium chloride (molecular weight 244) will have 122 grms. per litre; concentrated hydrochloric acid (molecular weight 36·5), of specific gravity 1·16, has 366 grms. per litre, and is therefore a "10E" solution. The same system was suggested by Reddrop in 1890. Reddrop (1890) recommended the designation "E," and Wollny (1885) the German equivalent "Aeq." The difference between an "E" solution and an "N" solution rests on the fact that a "normal" solution is supposed to be exact; the "equivalent" solution is approximate, and "rounded" atomic weights may be used in the calculations.

With this system, the amount of reagent needed for a specific purpose can be readily calculated and the addition of a great excess avoided. This means a saving in time, labour and material; and it indirectly leads to more accurate and reliable work. Thus, 1 c.c. of an "E" solution of sulphuric acid or any sulphate will very nearly suffice for the quantitative precipitation of the barium from 1 c.c. of an "E" solution of barium chloride. Again, suppose that 1 grm. of clay be fused with 7·5 grms. of sodium carbonate (molecular weight 106), and the cooled mass taken up with water and an excess of hydrochloric acid.

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[1] Ammonia and many other solutions are best kept in ceresine bottles or bottles lined with ceresine (ceresine is a white wax prepared from ozokerite)—O. Schreiner and G. H. Failyer, *Bull. U.S. Dept. Agric. (Soils)*, **31**, 20, 1906.

[2] R. Wollny, *Zeit. anal. Chem.*, **24**, 402, 1885; R. Blochmann, *Ber.*, **23**, 31, 1890; J. Reddrop, *Chem. News*, **61**, 245, 256, 1890.

Since 7·5 grms. of sodium carbonate correspond with a little less than one-seventh of an equivalent (53), the addition of 14·3 c.c. of 10 E-HCl will suffice to neutralise the sodium carbonate. Hence, say, 15 c.c. of the acid will be an excess. If the acid be evaporated down to dryness twice, in the regular manner, and the residue taken up the second time with 2 c.c. of the 10E-HCl, it will be obvious that 2 c.c. of 10E-NH$_3$ will suffice for the neutralisation of the acid, and 3 c.c. will be an excess of ammonia. This example shows how easily we can learn just how we stand with the quantities of the reagents present in our solutions. Measuring cylinders are useful for delivering definite volumes of the "E" solutions. Wollny recommends the use of pipette bottles,[1] by means of which definite volumes can be quickly measured.

The strengths of the acids and ammonia are easily obtained by means of the hydrometer and the tables in the Appendix. For example, take sulphuric acid. From gravity tables and the hydrometer we find that an acid of specific gravity 1·84 has 1759 grms. of H$_2$SO$_4$ per litre. Taking 49 as the equivalent of H$_2$SO$_4$, it follows that this acid is $\frac{1}{49}$ of 1759 = 36E strength. Obviously, 1 : 1 acid requires 500 c.c. of the concentrated acid per litre. The litre of the cold solution thus corresponds with 18E acid. If 5E acid be needed, the solution must contain 5 × 49 = 245 grms. of H$_2$SO$_4$ per litre. If 1759 grms. of H$_2$SO$_4$ correspond with a litre of the stock acid, 245 grms. of H$_2$SO$_4$ will correspond with 139·3 c.c. of the concentrated acid. This must be made up to a litre. In further illustration:—

Table XXII.— Strengths of Stock Acids and Ammonia.

Sulphuric acid, sp. gr. 1·84 = 36E.		Hydrochloric acid, sp. gr. 1·16 = 10E.		Nitric acid, sp. gr. 1·42 = 16E.		Ammonium hydroxide, sp. gr. 0·88 = 18·5E.	
E.	C.c. acid per litre.	E.	C.c. acid per litre.	E.	C.c. acid per litre.	E.	C.c. per litre.
20	557·2	..	..	..	..	..	..
10	278·6	10	1000	10	625	10	540
5	139·3	5	500	5	312·5	5	270
1	28·0	1	100	1	62·5	1	54

The concentrations of the reagents used in this work are given in the footnotes where the reagents are first mentioned. These can easily be located by reference to the index.

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[1] R. Wollny, *l.c.*; Warmbrunn and Quilitz, *Chem. Ztg.*, **17**, 454, 1893.

PART II.
TYPICAL SILICATE ANALYSES—CLAYS.

CHAPTER X.

THE DETERMINATION OF VOLATILE MATTERS.

§ 72. Hygroscopic Moisture.

The term "hygroscopic moisture" generally includes all the volatile constituents, principally moisture, which are given off when the substance is heated to a certain standard temperature, say, 110°.[1] The heating is continued until the substance ceases to lose weight. The ground [2] sample is placed in a stoppered weighing bottle of known weight. The bottle and contents are then weighed, and placed in an air bath [3] at the desired temperature. The stopper is removed, and a small filter-paper is fitted over the mouth of the weighing bottle to keep out the dust. The bottle and contents can be left in the oven overnight; the stopper of the weighing bottle is placed in the desiccator with the bottle; and, when cold, the stopper is inserted and the whole weighed. About four hours usually suffices for the drying, but, after weighing, the bottle is then returned to the air bath for another hour, and, when cold, re-weighed. If no further loss of weight occurs, the hygroscopic moisture of the clay in the bottle is represented by the total loss of weight which the clay has suffered on drying at 109° – 110°. The finely ground powder after drying is kept in the stoppered bottle, in a desiccator, for subsequent analysis.

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[1] Some heat the clay to 100°, but this is scarcely high enough; others work at 105° or 120°. For a rapid method for the determination of moisture in ceramic materials, see I. Ostoshevskii, *Ogneuporui*, **1**, No. 6, 40, 1933; *Chem. Zentr.*, (1), 3104, 1934.

[2] Most finely ground powders adsorb moisture so tenaciously that some is retained even after the powder has been heated to 110° an indefinitely long time. In fact, R. Bunsen (*Wied. Ann.*, **24**, 327, 1885), A. L. Day and E. T. Allen (*Amer. J. Science*, (4), **19**, 93, 1905) and J. T. Bottomley (*Chem. News*, **51**, 85, 1885) have shown that a red heat is required for the expulsion of all the adsorbed water.

[3] Either a toluene bath, fig. 58, or a bath fitted with a thermostat. Instead of toluene, a mixture of water and glycerol may be used: 6 parts of water to 1 of glycerol boils nearly at 105°; and a mixture of 1 part of water to 6 parts of glycerol, at 120°. Intermediate temperatures can be obtained by the use of intermediate mixtures. If the proportion of glycerol be increased much beyond the limit here mentioned, acrid fumes are given off— E. J. Reynolds, *Chem. News*, **4**, 319, 1861. An aqueous solution of calcium chloride, which boils at the desired temperature, can also be used, *e.g.* 100 grms. of water with 25 grms. of calcium chloride boils at 105°; with 41·5 grms., at 110°; with 69 grms., at 120°—G. T. Gerlach, *Zeit. anal. Chem.*, **26**, 413, 1887. Concentrated solutions of glycerol and calcium chloride sometimes cause trouble by attacking the joints of the bath, and require more attention owing to the gradual loss of water. When glycerol is used the mixture should be renewed after about 6 weeks, as there is a serious depression in boiling-point, probably due to polymerisation. Baths used for temperatures above 100° should be soldered with a high-melting solder such as "silver solder." We prefer an electrically-heated toluene bath. To prevent any escape of inflammable toluene vapours into the room, should the water of the condenser be turned off while the bath is going, a tube is fixed (*a*, fig. 58) from the top of the condenser to the outside of the laboratory.

One purpose of removing the hygroscopic moisture before the analysis is to secure a uniform hygroscopic condition as a basis for comparing the analytical data.[1] If an analysis were made on two samples of the same clay, one sample with 5 per cent. less hygroscopic moisture than the other, the silica in one might appear, in the statement of the analysis, as 60 per cent.,
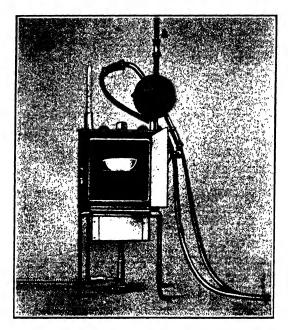
Fig. 58.—Toluene Bath at 109°–110°.

and in the other as 57 per cent. Hence, the analytical results will appear different according as the sample is collected in moist or in dry weather.

It is generally advisable, with commercial materials, to determine the amount of "hygroscopic moisture lost at 100°" or "at 110°."[2] For clays, it is best to use 109°–110°. Some materials are decomposed at this temperature. For example, superphosphates are liable to decompose at 110°. This is illustrated by the following determinations of the weights of acid calcium phosphate [3]—$CaH_4(PO_4)_2$—when heated one hour at the temperatures stated:

Temperature .	.	100°	105°	110°	120°	130°	140°	150°	160°	200°
Decomposition	.	0	2·0	4·3	4·9	6·6	8·4	13·3	17·7	50·4 per cent.

If the samples for analysis are received in paper or in canvas bags, it is not much use determining the hygroscopic moisture, because the result may be

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[1] See Z. A. James, *Eng. Min. Journ.*, 90, 1047, 1910.

[2] For the moisture retained by many salts dried in a steam oven—97°–98°—see H. W. Hake, *Proc. Chem. Soc.*, 13, 147, 1897; F. W. Smither, *Amer. Chem. Journ.*, 19, 227, 1897. 0·2864 grm. of calcium chloride, $CaCl_2$, after the 30th day, weighed 0·3200 grm.; 0·4349 grm. calcium nitrate, $Ca(NO_3)_2$, 0·4550 grm.; 0·1907 grm. magnesium chloride, $MgCl_2$, 0·2136 grm. The numbers varied a little according to the hygroscopic condition of the atmosphere. Obviously, therefore, we cannot consider drying in the steam oven, and possibly air baths, a sufficient means of standardising the hygroscopic condition of all materials.

[3] J. Stoklasa, *Zeit. anal. Chem.*, 29, 390, 1890; K. Birnbaum, *Zeit. Chem.*, (2), 14, 137, 1871. For white lead, see p. 328.

greater or less than when the sample was originally packed for the analyst. If the hygroscopic moisture is to be determined, the sample should be hermetically sealed in a vessel which will not allow an absorption or evolution of moisture. There are some "tricks" in sampling when the moisture question is left open.[1]

In order to distinguish between the moisture which has been absorbed by a given substance from its surroundings, and that which is given off by the decomposition of hydrated aluminium silicates or salts with water of crystallisation, at 110°, the substance is dried, not at 110° in an air bath, but at atmospheric temperatures in a desiccator over concentrated sulphuric acid— preferably *in vacuo*. This may occupy days or even weeks. The time can be shortened by drying the powder in a tube, in a current of air, dried by passage through, say, sulphuric acid, followed by phosphorus pentoxide. The loss in weight indicates the amount of moisture lost.[2] The moisture can be reabsorbed in a drying tube charged with phosphorus pentoxide, and the increase in its weight represents the moisture removed from the clay. This gives the hygroscopic moisture less the trace which the clay retains with remarkable tenacity, even at elevated temperatures.

The atmosphere in some air baths and steam ovens is quite humid, and contaminated with sulphurous gases, arising from the products of the combustion of the coal-gas beneath the oven. These gases find their way into the oven between the door and the front of the oven and may unite with the material being dried, thus interfering with the results, see p. 701. For example, several observers have noted that when thallic oxide is kept between 60° and 100° in an ordinary drying oven it increases in weight as it forms normal and acid thallous sulphates. If the burner gas be excluded the weight remains constant. A ledge is fixed vertically downwards on the front and on two sides of the oven, as shown in the diagram (fig. 58), and deflects the gases up the back of the oven, where they do no harm. There are also certain risks attending the use of ovens lined inside with metal. Dust from the corroded metal may fall on to the materials being dried. It is not difficult to line an oven with glazed porcelain or earthenware slabs, which can be obtained to fit the oven.[3]

It is important to place the thermometer near the weighing bottle, or a false idea is easily obtained as to the temperature of drying. Thus L. H. Bailey[4] tested a number of different ovens and found a very marked variation of temperature. For instance,

Table XXIII.—Fluctuations of Temperature in Drying Ovens.

Type of Oven.	Thermometer Reading.	Maximum Temperature Range.	
		Top shelf.	Bottom shelf.
Electrically-heated and controlled .	107°	99°–114°	90°–108°
Gas-heated, porcelain-lined . .	90°	88°– 92°	92°–102°
Gas-heated, air jacket . . .	100°	94°– 96°	105°–118°
Gas-heated, steam jacket . . . (Constant level water.)	98°	96°– 99°	95°–98°

[1] Spooner and Bailey, *Chem. News*, **21**, 21, 1870.
[2] When this experiment is done carefully, some very curious curves are obtained. Part of the water, usually thought to be "combined water," behaves as if it were "hygroscopic moisture"—E. Löwenstein, *Zeit. anorg. Chem.*, **63**, 69, 1909. See page 647.
[3] F. P. Treadwell, *Analytical Chemistry*, English translation by W. T. Hall, **2**, 24, 1919.
[4] L. H. Bailey, *Journ. Ind. Eng. Chem.*, **6**, 585, 1914; R. G. Grimwood, *Journ. Soc. Chem. Ind.*, **32**, 1040, 1913.

Hence, adds Bailey, "Elaborately designed and expensive ovens are no more reliable than the more simple and inexpensive types. Of the ovens tested, only those surrounded by boiling water and steam were capable of maintaining even an approximately uniform temperature." To these might be added ovens jacketed with vapours other than steam, *e.g.* toluene, and heated by gas or the electric current.

§ 73. Loss on Ignition.

This term is used to represent the total loss in weight which occurs when the clay is calcined at a bright red heat. The "loss on ignition" may thus include the loss in weight which attends the expulsion of water (page 641) formed during the decomposition of the clay; carbon dioxide from carbonates (page 625); sulphurous gases from sulphates, and the oxidation of sulphides; [1] the combustion of carbon and organic matter (page 631); the volatilisation of ammonium compounds and alkalies. The loss in weight on ignition is usually great enough to mask the gain in weight which occurs during the more or less incomplete oxidation of ferrous to ferric and magnetic oxides and manganese compounds to Mn_3O_4. However, it is not uncommon to find firebricks which *gain* up to 0·5 or even 1·0 per cent. on ignition. This is probably due to the oxidation of ferrous and metallic iron. Sometimes these bricks, when powdered and treated with acids—dilute hydrochloric acid, for instance—give off hydrogen gas, showing the presence of metallic iron. [2] The loss on ignition is not always satisfactory for exact investigations, [3] but for industrial purposes it sometimes indicates what is likely to happen when a clay is fired in ovens or kilns.

To determine the loss on ignition, about 1 grm. [4] of the clay is calcined in a weighed platinum crucible which has been ignited recently to a red heat, and cooled in a desiccator. The crucible, during the earlier stages of the ignition, is inclined 30°–45° on a platinum or silica triangle, as indicated in fig. 59. The flame is so arranged that it does not envelop the whole crucible, but impinges on one side, thus allowing the air to circulate freely about the mouth of the crucible. Some clays, ball clays in particular, must be heated very slowly at first, or fine particles of clay will be carried away from the crucible with currents of gas and steam. A blast is usually needed for the later stages of the ignition. [5] A crucible is shown in fig. 60 being heated over a blast. After the clay has been blasted about 10 minutes, the crucible is allowed to cool down to a temperature below red heat. It is then lifted into the desiccator by means of a pair of platinum-tipped tongs, allowed to cool and weighed. Again blast the crucible and contents 5 minutes, cool and weigh as before. If a further loss in weight takes place, the blasting must be repeated until two successive weighings are approximately constant.

[1] The sulphur may be retained by free lime, etc., if present in the form of sulphur trioxide. For sulphur and chlorine losses during ignition, see J. O'Sullivan, *Analyst*, 39, 425, 1914; for phosphorus, see p. 688.

[2] F. Stolba (*Zeit. anal. Chem.*, 7, 93, 1868) shows that a correction can be made if the amount of ferrous oxide be determined, because one gram of this oxide increases by 0·1111 grm. on passing to the ferric condition.

[3] For the direct determination of water, carbon, carbon dioxide, etc., see later chapters.

[4] If the clay be not very hygroscopic, exactly 1 grm. may be weighed out. This saves trouble in calculations, but it is necessary to guard against the error mentioned on page 45.

[5] Alkalies begin to escape at a red heat. Potassium usually comes off faster than sodium. The alkalies, after a long blasting, may be found partly condensed on the lid. If the blasting be long continued, most of the alkalies will be volatilised in this way. If the ignition temperature be properly adjusted, the loss of sulphur and alkalies is inappreciable.

Fig. 59.—Ignition over a Méker's Burner.
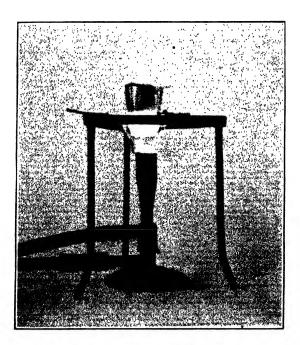
Fig. 60.—Ignition over a Blast Méker's Burner.

Highly carbonaceous clays are sometimes advantageously mixed with a known weight of ignited magnesia to prevent the fusion or agglomeration of the residue during ignition.[1]

Errors.—Determinations of the loss on ignition of eight portions of one sample of powdered clay, each weighing 1 grm., gave the following numbers: 0·0927, 0·0933, 0·0927, 0·0931, 0·0931, 0·0930, 0·0929, 0·0930 grm., with a mean of 0·0930 grm., that is, 9·30 per cent., and a maximum and minimum deviation of ±0·03. These numbers give us an idea of the differences which might be expected in duplicate determinations. If another analyst made a determination, his result ought not to differ by much more than ⊣ 0·03 from 9·30 per cent. If it did, one of the results is wrong, or the sampling is faulty, or the "drying temperature" is different from 110°.

The chief sources of error arise from: (1) Imperfect drying (hygroscopic moisture); (2) Oxidation or reduction of ferrous iron, etc.; (3) Imperfect expulsion of water owing to a too low temperature of ignition;[2] (4) More or less imperfect decomposition or volatilisation of some of the constituents, *e.g.* fluorides,[3] sulphates;[4] and (5) Mechanical loss of the substance by the transport of fine particles along with the steam when the temperature is raised too rapidly.[5]

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[1] A. Müller (*Journ. prakt. Chem.*, (1), 80, 118, 1860) mixes ferric nitrate with the powdered material. According to A. Gutbier (*Chem. Ztg.*, 34, 211, 1910), W. C. Heraeus has designed a perforated crucible lid with a partition extending into the crucible. By heating one side of the crucible a circulation of air is induced which is said to facilitate the combustion of organic matter.

[2] Some minerals—*e.g.* talc and steatite—require a high blasting temperature to drive off all the water—T. Scheerer, *Pogg. Ann.*, 84, 321, 1851.

[3] K. List, *Liebig's Ann.*, 81, 189, 1852.

[4] C. R. Fresenius (*Quantitative Chemical Analysis*, London, 1, 55, 1876) says the loss of sulphur trioxide from sulphates can often be guarded against by adding finely divided, recently ignited lead monoxide, equal in amount to about six times the weight of the substance.

[5] G. Cesaro, *Mém. Soc. Roy. Sciences Lièges*, (3), 5, 1, 1906.

CHAPTER XI.

OPENING-UP SILICATES.

§ 74. Summary of the Different Methods.

SOME silicates are easily decomposed by more or less prolonged digestion in acids; others require a more drastic treatment. Some, apparently insoluble silicates, decompose in acids after a preliminary calcination at 500°–600°. Certain other substances, on the contrary, become less soluble on calcination;[1] an internal change occurs attended by the evolution of heat, so much so that the mass, as J. J. Berzelius records,[2] exhibits a vivid incandescence which begins at a point and extends throughout the entire mass. A great variety of methods has been proposed and used for the opening up of silicates preparatory to analysis.[3] Many of these methods are now obsolete. Although the sodium carbonate fusion is generally used, some of the other methods are invaluable in special cases. A number of methods are indicated below; others will be described later in connection with glazes and glasses, also chromite and uranium.

I. *Silicates decomposed by Digestion with Mineral Acids.*—Sulphuric, hydrochloric, or nitric acid, or mixtures of these acids—in open vessels or sealed tubes.

(a) Natural silicates. Used for the so-called "rational analysis"; analysis of slags, some lead frits, etc. See pages 509, 753 *et seq.*

(b) After the silicate has been calcined at a dull red heat, below the melting-point of the silicate.[4] *E.g.* tourmaline in hydrofluoric acid; axinite, garnet, and vesuvian in hydrochloric acid. See page 510.

(c) After exposure to reducing gases at a dull red heat. See page 266.

(d) Digestion with hydrochloric or sulphuric acid in sealed tubes, under pressure.[5] See page 551.

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[1] *E.g.* zirconia, titanic acid, tantalic acid, molybdic oxide, alumina, chromic oxide, ferric oxide, rhodium oxide, basic ferric arsenate, copper antimonate, euxenite, gadolinite. L. Gmelin, *Handbook of Chemistry*, London, **1**, 107, 1848; T. Scheerer, *Pogg. Ann.*, **51**, 493, 1840; F. von Kobell, *Journ. prakt. Chem.*, (1), **1**, 91, 1834.

[2] J. J. Berzelius, *Lehrbuch der Chemie*, Dresden, **1**, 841, 1825.

[3] For the decomposition of chromite, see page 527; and for ferruginous minerals, page 511.

[4] F. Mohr, *Zeit. anal. Chem.*, **7**, 293, 1868; F. Rocholl, *ib.*, **20**, 289, 1881; C. Rammelsberg, *Pogg. Ann.*, **80**, 457, 1850; H. Rose, *ib.*, **108**, 1, 1859; G. Magnus, *ib.*, **20**, 477, 1830; **21**, 50, 1831; **22**, 391, 1831; H. Hess, *ib.*, **45**, 341, 1838; F. Varrentrapp, *ib.*, **45**, 343, 1838; see page 511, FeO.

[5] A. Mitscherlich, *Journ. prakt. Chem.*, (1), **81**, 108, 1860; **83**, 455, 1861; P. Jannasch, *Ber.*, **24**, 2734, 3206, 1891; *Zeit. anorg. Chem.*, **6**, 72, 1894; F. C. Phillips, *Zeit. anal. Chem.*, **12**, 189, 1873; V. D. Voznesenskii *et al.*, *Zavodskaya Lab.*, **2**, 37, 1933.

II. *Silicates decomposed by Hydrofluoric Acid alone or by a Fluoride mixed with a Mineral Acid.*—Sulphuric, hydrochloric, or nitric acid.

(*a*) Vapour at a red heat.[1]

(*b*) Aqueous solution alone or with mineral acids.[2] This process is much used for the determination of ferrous iron and alkalies, etc.

(*c*) Digestion with a fluoride mixed with an acid or some salt which decomposes the fluoride.

  (i) Ammonium fluoride and sulphuric acid.[3]
  (ii) Potassium hydrogen fluoride.[4]
  (iii) Calcium fluoride and sulphuric acid.[5]
  (iv) Sodium fluoride with an acid or with potassium bisulphate.[6]
  (v) Barium fluoride with an acid or with barium nitrate.[7]

III. *Silicates decomposed by Fusion with Alkali Oxides or Salts.*—This method is not usually applied if the silicate is decomposed by simple treatment with acids, in open vessels.

(*a*) Fusion with alkali hydroxides. Fused caustic potash and soda ash were among the earliest fluxes in use for decomposing silicates.[8] Pure sodium carbonate and caustic soda are now much used for opening up silicates.[9]

(*b*) Fusion with sodium peroxide. This is much used for opening up chromites and hæmatites, as described on pages 264, 527, etc. The violence of the action may be tempered by mixing the peroxide with sodium hydroxide or lime.

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[1] A. Brunner, *Pogg. Ann.*, **44**, 134, 1838; F. Kuhlmann, *Compt. rend.*, **58**, 545, 1864; A. H. Allen, *Analyst*, **21**, 87, 1896; A. Müller, *Journ. prakt. Chem.*, (1), **95**, 51, 1865.

[2] J. J. Berzelius, *Pogg. Ann.*, **1**, 169, 1824; H. Rose, *Liebig's Ann.*, **72**, 324, 1849; D. D. Craig, *Chem. News*, **60**, 227, 1889; E. Linnemann, *ib.*, **52**, 220, 233, 240, 1885; N. S. Maskelyne, *ib.*, **21**, 27, 1870; *Proc. Roy. Soc.*, **18**, 147, 1869; F. Hinden, *Zeit. anal. Chem.*, **25**, 332, 1906; A. Thürmer, *Keramos*, **10**, 657, 1931; J. Delforge, *Bull. Soc. chim. Belg.*, **39**, 539, 1930.

[3] L. von Babo, *Amt. Ber. deut. Naturforscher. Aertze Mainz*, **20**, 103, 1842; J. Potyka, *Untersuchungen über einige Mineralien*, Berlin, **38**, 1859; H. Rose, *Pogg. Ann.*, **108**, 20, 1859; R. Hoffmann, *Zeit. anal. Chem.*, **6**, 367, 1867; *Chem. News*, **17**, 24, 1868. The ammonium fluoride should leave no residue when evaporated to dryness. P. T. Austen and F. Wilber (*Chem. News*, **48**, 274, 1883) purify by dissolving commercial ammonium fluoride in as little water as possible in a platinum dish (or, better, place hydrofluoric acid in a platinum dish), and adding an excess of concentrated ammonia slowly from a pipette to avoid loss by spurting. A voluminous precipitate may separate. Decant the clear liquid for use. In silicate decompositions, acidify the solution with sulphuric acid and evaporate to dryness.

[4] C. Marignac, *Ann. Chim. Phys.*, (4), **8**, 115, 1866; W. Gibbs, *Amer. J. Science*, (2), **37**, 357, 1864; *Chem. News*, **10**, 37, 49, 1864; F. A. Clarke, *Zeit. anal. Chem.*, **7**, 463, 1868.

[5] C. E. Avery, *Chem. News*, **19**, 270, 1869; C. A. Wilbur and W. Whittlesey, *ib.*, **22**, 2, 1870.

[6] F. W. Clarke, *Amer. J. Science*, (2), **45**, 173, 1868; (3), **18**, 290, 1877; *Chem. News*, **17**, 232, 1868; C. E. Avery, *ib.*, **19**, 270, 1869.

[7] G. Gore, *Journ. Chem. Soc.*, **15**, 104, 1863; C. E. Avery, *Chem. News*, **19**, 270, 1869.

[8] M. H. Klaproth, *Analytical Essays*, London, **1**, 50, 1801; E. Büttner, *Silikat-Zeit.*, **2**, 149, 1914; C. J. van Nieuwenburg and H. H. Dingemans, *Chem. Weekb.*, **25**, 266, 1928; S. R. Scholes (*Glass Ind.*, **11**, 164, 1930) uses 1 grm. of sodium hydroxide and 3 grms. of sodium nitrate per 0·5 grm. of the sample and fuses for 1 hour at 300°.

[9] M. W. Iles, *Eng. Min. Journ.*, **31**, 58, 1881; *Chem. News*, **43**, 78, 1881; C. A. Burghardt, *ib.*, **61**, 260, 1890; *Proc. Manchester Lit. Phil. Soc.*, (4), **3**, 171, 1890; W. Mylius, *Kerum. Rund.*, **40**, 33, 1932. See page 264.

(c) Fusion with alkali carbonates. Marggraf[1] seems to have been one of the first to mention the use of fusion with alkali carbonates in analysis.

    (i) Sodium carbonate.[2]

    (ii) Fusion mixture.[3]

    (iii) Sodium bicarbonate.[4]

    (iv) Potassium carbonate.[5] This salt is sometimes preferred to sodium carbonate—e.g. with tungstates, columbates, tantalates—on account of the greater solubility of the potassium salt.

    (v) Lithium carbonate.[6]

(d) Potassium or sodium bisulphate or pyrosulphate.[7] Smith prefers the sodium salt in certain cases—e.g. in the decomposition of corundum—since the double salt of aluminium and potassium is dissolved with greater difficulty under conditions where the sodium salt is freely soluble.

IV. *Calcining the Silicate with an Alkaline Earth.*—Oxide, carbonate, etc.

(a) Calcium carbonate or oxide, alone or with calcium chloride.[8]

(b) Calcium carbonate with ammonium chloride.[9]

(c) Calcium sulphate.[10] This was used by von Hauer for lepidolite.

(d) Barium oxide or carbonate or nitrate.[11]

(e) Calcium fluoride with or without sulphuric acid.[12]

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[1] A. S. Marggraf, *Chemische Schriften*, Berlin, 2, 135, 1767. For the action between sodium carbonate and various oxides at about 1000° C., see A. Romwalter, *Mitt. berg. hüttenmänn. Abt. ungar. Hochschule Berg.-Forstw. Sopron*, 5, 38, 1933.

[2] S. Kern, *Chem. News*, 35, 203, 1877; D. Lindo, *ib.*, 60, 14, 33, 41, 1889; L. H. Freidburg, *ib.*, 62, 22, 32, 1890; *Journ. Amer. Chem. Soc.*, 12, 134, 1890; J. A. L. W. Knop, *Leipzig Maths. Phys. Ber.*, 34, 33, 1882; *Zeit. anal. Chem.*, 22, 558, 1883; *Chem. News*, 49, 62, 1884; E. Mallard, *Ann. Chim. Phys.*, (4), 28, 86, 1873; A. Thürmer, *Keramos*, 10, 657, 1931. F. Stolba (*Sitzber. könig. Böhm. Ges. Wiss.*, 1885; *Zeit. anal. Chem.*, 25, 378, 1886) recommends placing a layer of sodium chloride over the charge in the crucible before the mixture is heated.

[3] See page 143. C. F. Chandler, *Pogg. Ann.*, 102, 446, 1857.

[4] C. Holthof, *Zeit. anal. Chem.*, 23, 498, 1884; *Chem. News*, 51, 18, 1885.

[5] H. Rose, *Ausführliches Handbuch der analytischen Chemie*, Braunschweig, 2, 630, 1852; J. J. Berzelius, *Pogg. Ann.*, 4, 152, 1824; W. B. Giles, *Chem. News*, 99, 25, 1909; M. H. Bedford, *Journ. Amer. Chem. Soc.*, 27, 1216, 1905; A. F. Gehlen, *Schweigger's Journ.*, 6, 258, 1812; A. S. Marggraf, *Chemische Schriften*, Berlin, 2, 135, 1767.

[6] R. Schwartz and A. Schinzinger, *Zeit. anorg. allgem. Chem.*, 151, 214, 1926; J. Kühnhold, *Glashutte*, 64, 587, 1934; J. E. Gieseking and H. J. Snider, *Ind. Eng. Chem. Anal. Ed.*, 9, 233, 1937.

[7] J. L. Smith, *Amer. J. Science*, (2), 40, 248, 1865; *Chem. News*, 12, 220, 1865; W. H. Worthington, *Min. Science*, 63, 521, 1911.

[8] S. F. Glinka, *Journ. Russ. Chem. Soc.*, 24, 456, 1892; L. R. von Fellenberg-Rivier, *Zeit. anal. Chem.*, 5, 179, 1866; H. Cormimbeuf, *Ann. Chim. anal.*, 15, 295, 1910; H. St C. Deville, *Ann. Chim. Phys.*, (5), 61, 309, 1861; *Chem. News*, 4, 255, 1861; E. Bonjean, *ib.*, 80, 240, 1899; H. Rocholl, *ib.*, 41, 234, 1880.

[9] J. L. Smith, *Amer. J. Science*, (2), 50, 269, 1871.

[10] F. Stolba, *Zeit. anal. Chem.*, 16, 99, 1877.

[11] G. Werthier, *Journ. prakt. Chem.*, (1), 91, 321, 1864; H. Abich, *Pogg. Ann.*, 50, 128, 341, 1840; P. Berthier, *ib.*, 14, 100, 1828; J. W. Döbereiner, *ib.*, 14, 100, 1828; L. R. Fellenberg-Rivier, *Zeit. anal. Chem.*, 9, 459, 1870; W. Hempel, *ib.*, 52, 86, 1913; G. Gore, *Journ. Chem. Soc.*, 15, 104, 1862; J. J. Berzelius, *De l'Analyse des Corps Inorganiques*, Paris, 72, 1827; M. H. Klaproth, *Beiträge zur Kenntniss der Mineralkörper*, Berlin, 3, 240, 1802.

[12] G. Scheffer, *Liebig's Ann.*, 109, 144, 1859; C. A. Joy, *Chem. News*, 8, 183, 197, 1863; *Amer. Journ. Science*, (2), 36, 83, 1863.

V. *Fusion with Lead or Bismuth Compounds.*

(*a*) Lead oxide.[1]   This method is sometimes used in determining the total water in clay by Jannasch's process.   The lead oxide retains fluorine and boron.

(*b*) Lead carbonate.[2]

(*c*) Lead chromate.[3]

(*d*) Fusion with bismuth oxide or nitrate.[4]

VI. *Fusion with Sodamide*, $NaNH_2$.

A large variety of natural and artificial silicates, such as clay, felspar, serpentine, soapstone, fired refractories, glasses and also bauxite, are completely decomposed by fused sodamide.   Fusion for 2–3 hours at 330° is recommended, and it is claimed that nickel instead of platinum crucibles can be used as less than 0·3 mgrm. of nickel passes into the fusion.[5]

VII. *Fusion with Boron Compounds.*

(*a*) Boric oxide, or boric acid.[6]   This process promises to be useful for the determination of silica in the presence of fluorides, since, it is stated, the fluorine is evolved as boron fluoride—BF_3— not as silicon fluoride—SiF_4.

(*b*) Borax.[7]   Chenevix found that he could not open corundum by fusion with potash or soda, but he succeeded by fusing the mineral with borax. According to Wells, borax and boric anhydride attack platinum quite appreciably during high-temperature fusions.

(*c*) Potassium borofluoride mixed with potassium carbonate.[8]   This mixture was used by Stolba for opening up zircons (4 of flux, 1 of powdered zircon).

VIII.—*Heating in Vapours of*

(*a*) Sulphur monochloride—page 561.

(*b*) Carbon tetrachloride.[9]

[1] P. Berthier, *Ann. Chim. Phys.*, (2), **17**, 28, 1821; G. Bong, *Zeit. anal. Chem.*, **18**, 270, 1878; P. Jannasch and H. J. Locke, *Zeit. anorg. Chem.*, **6**, 168, 321, 1894 (for topaz); A. Leclerc, *Compt. rend.*, **125**, 893, 1897; *Chem. News*, **77**, 27, 1898; C. A. Joy, *Amer. Journ. Science*, (2), **36**, 83, 1863; *Chem. News*, **8**, 183, 197, 1863.

[2] P. Jannasch, *Ber.*, **26**, 1497, 2909, 1893; **27**, 2228, 1894; *Zeit. anorg. Chem.*, **8**, 364, 1893; *Chem. News*, **71**, 51, 1895.

[3] P. Jannasch, *Ber.*, **22**, 221, 1889.

[4] W. Hempel and R. F. Koch, *Zeit. anal. Chem.*, **20**, 496, 1881; *Chem. News*, **45**, 81, 1882 (nitrate); T. M. Chatard, *Amer. J. Science*, (3), **29**, 379, 1889; *Chem. News*, **50**, 279, 1884 (oxide).

[5] P. V. Petersen and F. W. Bergstrom, *Ind. Eng. Chem. Anal. Ed.*, **6**, 136, 1934.

[6] H. Davy, *Phil. Trans.*, **85**, 231, 1805; P. Jannasch, *Ber.*, **28**, 2822, 1896; P. Jannasch and O. Heidenreich, *Zeit. anorg. Chem.*, **12**, 208, 219, 1896; P. Jannasch and H. A. Weber, *Ber.*, **32**, 1670, 1899; H. A. Weber, *Ueber die Aufschliessung der Silikate durch Borsäureanhydrid*, Heidelberg, 1900; K. Pfeil, *Ueber die Aufschliessung der Silikate und anderer schwer zersetzbar Mineralien mit Borsäureanhydrid*, Heidelberg, 1901; E. Rupp and F. Lehman, *Chem. Zig.*, **35**, 565, 1911; A. Thürmer, *Keramos*, **10**, 657, 1931; F. Specht, *Zeit. anorg. allgem. Chem.*, **231**, 181, 1937.

[7] C. Rammelsberg, *Zeit. deut. geol. Ges.*, **24**, 69, 1872; W. Suida, *Tschermak's Mitt.*, (1), **5**, 176, 1876; *Zeit. anal. Chem.*, **17**, 212, 1878; J. S. C. Wells, *School Mines Quart.*, **12**, 295, 1891; *Chem. News*, **64**, 294, 1891; R. Chenevix, *Journ. de Phys.*, **55**, 409, 1802.

[8] F. Stolba, *Chem. News*, **49**, 174, 1884.

[9] S. J. Johnstone, *Min. Mag.*, **16**, 226, 1912.

IX. *Electrical Current.*—Several attempts have been made to decompose certain silicates and minerals while exposed to the joint effect of acids and an electric current, but with success only in special cases.[1]

§ 75. Sodium Carbonate for Silicate Fusions.

In most silicate analyses, the mineral is broken down by fusion with anhydrous sodium carbonate—a plan first used by T. Bergmann in the eighteenth century. Obviously, the sodium carbonate must be free from impurities which have to be determined in the fused silicate.[2] For instance, if sulphur is to be determined, the carbonate must be free from sulphur compounds. The total impurities—silica, alumina, etc.—should not exceed 0·01 per cent. If 10 grms. of this carbonate be taken for the analysis, the maximum error for the impurities in it will not then exceed 0·1 per cent. The impurities can be determined by a blank analysis.

Fig. 61.—Melting-Points of Mixtures of Sodium and Potassium Carbonates.

Potassium carbonate fuses at about 888°, and sodium carbonate at 851°,[3] while a mixture with about 46 grm.-molecules per cent. of potassium carbonate melts at 712°. The freezing-point curve for all liquid mixtures is indicated by the solid line in fig. 61 and the melting-point curve for the corresponding solid mixtures by the broken line. The so-called "fusion mixture" (sodium carbonate, 4·5 parts by weight; potassium carbonate, 5 parts) is the most fusible mixture of these two carbonates. Hence, this mixture is sometimes recommended for opening up silicates in preference to sodium carbonate alone, because of its greater fusibility. This point is, however, of little importance, because the temperature of silicate fusions is generally greater than the melting-point of either salt alone; and there is no difficulty in maintaining the necessary temperature.

Dittrich[4] has pointed out that potassium salts are washed from the different precipitates, later on, with greater difficulty than sodium salts. In illustration, Reidenbach shows that a "magnesia" precipitate made in a 3N solution of potassium chloride retains nearly twice the weight of occluded salt as a precipitate made under similar conditions in a 3N solution of sodium chloride. Still further, Smith has shown that the resulting cake with potassium carbonate dissolves in water with greater difficulty than when sodium carbonate is used.

[1] E. F. Smith, *Ber.*, 23, 2276, 1890; 25, 152, 1892; L. F. Frankel, *Chem. News*, 65, 54, 66, 1892; M. Mayençon, *ib.*, 76, 24, 1897.

[2] See J. L. Smith (*Chem. News*, 30, 234, 1874) on the preparation of pure potassium and sodium carbonates for silicate fusions. Excellent sodium carbonate can now be purchased with a guaranteed composition.

[3] P. Niggli, *Zeit. anorg. Chem.*, 106, 126, 1919.

[4] M. Dittrich, *Anleitung zur Gesteinanalyse*, Leipzig, 5, 1905; R. Reidenbach, *Ueber die quantitative Bestimmung des Magnesiums als Magnesiumpyrophosphat*, Kusel, 69, 1910.

Platinum crucibles are slightly attacked by the fusion with sodium carbonate. Koninck [1] says that 6 grms. of fusion mixture when melted in a platinum crucible over a Bunsen burner, and then over a blast, caused the platinum crucible to lose in weight 0·0010 grm. Hence, Koninck says that in exact analyses the platinum should be removed by treatment with hydrogen sulphide in acid solution. Koninck's numbers are higher than those obtained in our own experience with sodium carbonate fusions. There is also no need to remove the platinum until after the potassium bisulphate fusion, as indicated on page 168.

§ 76. Opening Clays and Silicates by Fusion with Sodium Carbonate.

Charging the Crucible.—Either 1 grm. of the powdered clay dried at 110°, or the clay remaining in the crucible after the loss on ignition [2] has been determined, is mixed with six to eight times its weight of anhydrous sodium carbonate, by adding the carbonate to the crucible and thoroughly mixing the contents of the crucible by means of a spatula, care being taken to get plenty of sodium carbonate at the bottom of the crucible. Two more grams of sodium carbonate are introduced and levelled down with the spatula. The spatula is also cleaned by the sodium carbonate at the same operation.

The Fusion.—The crucible is placed slightly inclined on a platinum or pipe-clay triangle, so that the flame does not completely envelop the crucible. The object is to keep the atmosphere inside the crucible as oxidising as possible. The lid is placed on the crucible, and the latter is heated over a low flame with the bottom of the crucible at a dull red for a quarter of its length. This drives off the carbon dioxide without spluttering. In about 15 minutes the crucible is heated to bright redness by means of, say, a Teclu or a Méker burner for another 15 minutes. The contents of the crucible will then probably be in a state of quiet fusion [3] and gas bubbles will have ceased to come off. Little if any spluttering of the contents of the crucible on to the inside of the lid will have taken place if the operation has been properly performed.

Cooling the Crucible.—The crucible is then removed from the flame by the platinum-tipped tongs and allowed to cool on a slab of granite, marble or an unglazed tile.[4] A green-coloured cake indicates the presence of manganese—sodium manganate—but manganese may be present without showing the green colour if the inside of the crucible, during the fusion, was not sufficiently oxidising. The dirty brown colour of highly ferruginous clay may also obscure the manganese green.

Transfer of the Cake to the Basin.—When cold, the crucible is half filled with water, and a gentle heat applied without allowing the contents to boil. If the crucible be not dented, and has been allowed to cool a sufficient length of time, the cake will quickly loosen *en bloc*,[5] and may be tipped into a *dry* 350 c.c.

[1] L. L. de Koninck, *Zeit. anal. Chem.*, 18, 569, 1879.

[2] If the clay sinters into clots when the loss on ignition is determined, it is best to work with an uncalcined sample, because sintered masses are decomposed with difficulty by the fused carbonate.

[3] Highly siliceous clays, flint and felspar usually give clear transparent fusions; while Cornish stone, clays and pottery bodies, even though completely decomposed, form more or less turbid liquids. Highly aluminous clays form viscid liquids and siliceous clays limpid liquids. It is a good plan to use rather more sodium carbonate for the former type of silicate.

[4] R. Howden (*Chem. News*, 107, 232, 1913) adds a pinch of powdered nitre to the still molten mass. The evolved gases make the cake more porous and easier to detach from the crucible.

[5] Do not "squeeze the platinum crucible between the finger and thumb to loosen the fused mass," as one writer recommends.

evaporating basin[1] glazed on the *inside* only.[2] About 150 c.c. of water[3] are added to the cake, the basin is covered with a clock glass and about 20 c.c. of concentrated hydrochloric acid[4] introduced from a pipette through the lip of the basin. When the first violent reaction is over, the basin is warmed on a water bath until all action has ceased and the cake has disintegrated. The clock glass is now removed and any drops on the underside of it are rinsed into the basin. The platinum crucible and lid are next washed with dilute hydrochloric acid and hot water and the washings poured into the basin. The cake is now crushed to powder with a small agate pestle. Any white spots which appear on the crucible[5] after it has been cleaned and dried must be transferred to the basin.

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[1] To mark porcelain vessels, scratch a mark on the vessel with a diamond. Smear platinic chloride over the mark, and when it is almost dry wipe (not wash) it off. When fired in a muffle, the vessel is marked with metallic platinum (B. Blount, *Chem. News*, 56, 66, 1887; A. A. Kelly, *ib.*, 83, 95, 1901). H. Jervis (*Chem. News*, 83, 118, 1901) recommends marking crucibles with ink, and W. C. Kriescher (*Chem. News*, 83, 130, 1901) with blue pencils and then firing. C. Reinhardt (*Zeit. anal. Chem.*, 23, 42, 1884) recommends marking in coloured enamel, finely powdered, and ground in aniseed or lavender oil. This is marked on the porcelain and fired in a muffle. P. A. Yoder, *Chem. Eng.*, 15, 102, 1911; *Journ. Ind. Eng. Chem.*, 4, 567, 1912; C. D. Mason, *ib.*, 4, 691, 1912. M. Liebschultz (*Chem.-Analyst*, 9, 11, 1914) adds a little platinic chloride to ordinary marking ink and writes with a pen. After ignition the mark is permanent. S. B. Kurizian (*Journ. Ind. Eng. Chem.*, 8, 89, 1916) uses cobalt nitrate.

[2] The rate of evaporation from basins which are glazed on the inside and on the external rim only, is from 50 to 100 per cent. quicker than from basins which are glazed all over.

[3] Analysts are frequently puzzled why the silica from a given silicate fusion is sometimes gelatinous and difficult to filter and wash, and at other times it appears more or less pulverulent and easy to wash. In many cases this is due to the way the fused cake in the crucible is treated. The pulverulent form is obtained by dissolving the cake in a large volume of water, say 200 c.c., and then acidifying the solution. This large volume may take longer to evaporate than when the acid is added to a concentrated solution; but if the concentrated solution be acidified, the silica is more likely to separate in the gelatinous form. In the latter case, a considerable amount of time will be spent in filtering and washing, and the result will be less satisfactory. The silica which separates from the dilute solutions also appears to be of greater purity. When the silica separates from concentrated solutions, it probably encloses particles of liquid not easily removed by washing. These results are not so marked when considerable amounts of alumina are present, but in any case the different effects are noticeable—D. Lindo, *Chem. News*, 60, 14, 33, 41, 1889. Some consider that the addition of alcohol to the solution makes the silica separate during evaporation in the granular form, which is easily filtered and washed. It is also claimed that two evaporations are not then necessary.

[4] H. H. Willard and W. E. Cake (*Journ. Amer. Chem. Soc.*, 42, 2208, 1920) and W. K. Gibson (*Rocks Products*, 35, 70, 1930) recommend the use of concentrated perchloric acid instead of hydrochloric acid; the process is quicker, less silica passes into solution (see page 152), and it is separated in a purer state. See also F. H. Fish and F. M. Taylor, *Journ. Chem. Educn.*, 10, 246, 1933.

[5] The less dented and the smoother the crucible, the more easily is the cake removed. A very obstinate cake is dissolved in the crucible on the water bath, with or without the addition of hydrochloric acid, and the contents emptied from time to time into the evaporating basin. Fresh water or acid is introduced into the crucible. If the acid be used with a green cake, chlorine may be evolved and attack the crucible. In that case, a few drops of alcohol will destroy the manganate, and prevent the generation of chlorine. F. Stolba (*Zeit. anal. Chem.*, 25, 378, 1886) pours the melted mass on a suitable slab; J. Herman (*West. Chem. Met.*, 5, 476, 1909) pours the melted mass into a beaker containing 50 c.c. of water. In that case, the mass should be a limpid fluid when poured, or an explosion might result. Bisulphate and caustic alkali fusions must not be poured into water. L. L. de Koninck (*Zeit. angew. Chem.*, 1, 569, 1888) recommends inserting a piece of platinum wire, bent at one end in the form of a spiral, into the fused mass when fusion is complete; when cold, the other end of the platinum wire is suspended from a glass rod, or a retort clamp, so that the crucible hangs a few millimetres above the triangle. On heating the crucible quickly, the crucible falls into the triangle and the "melt" remains suspended on the platinum wire separated from the crucible. Both it and the residue in the crucible can then be dissolved in the regular manner—E. R. E. Müller, *Chem. Ztg.*, 32, 880, 1908.

The cake will not dissolve very readily if the fusion has been conducted at a very high temperature. Flakes of silicic acid may now be observed floating about the liquid. If any gritty particles remain in the basin, the decomposition by the sodium carbonate was not complete.[1] In that case it is best to start again.[2]

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[1] Magnetite and ilmenite may escape decomposition by the fusing carbonate, and yet be subsequently dissolved by the hot hydrochloric acid. According to P. W. Shimer (*Journ. Amer. Chem. Soc.*, 16, 501, 1894) in the analysis of blast-furnace slag, spinel—magnesium aluminate—is not decomposed by fusion with alkali carbonates. By treating the slag with hydrochloric and hydrofluoric acids, and afterwards boiling the residue with sodium carbonate, the spinel can be isolated as a crystalline powder. Treatment with concentrated sulphuric and hydrofluoric acids decomposes the spinel. This substance, therefore, if present, will be broken down at a later stage of the analysis—correction for silica.

[2] If the amount of sample available be small, the undecomposed material can be collected in a filter-paper, ignited and re-fused with sodium carbonate.

CHAPTER XII.

THE DETERMINATION OF THE SILICA.

§ 77. The Determination of Silica.

First Evaporation.—The hydrochloric acid solution of the cake contains the various constituents of the clay in solution principally as chlorides. These are subsequently removed one by one. First the silica. Evaporate[1] the contents of the basin to dryness on the water bath, protected from dust.[2] There is no appreciable loss of the constituents to be determined in the solution during the evaporation.[3] Heat the dry residue in an oven (fig. 58), between 109° and 110°, or leave it on the water bath, until the smell of the hydrochloric acid has disappeared.[4] Pour about 5 c.c. of concentrated hydrochloric acid and 30 40 c.c. of water on the residue; warm on a water bath 10 to 15 minutes; break up any coarse lumps with a glass rod; decant the clear liquid into, say, a 9 cm. filter-paper, and collect the filtrate in a 400 c.c. beaker. Add more water and acid to the basin, warm again; again decant through the filter-paper, repeat the treatment, and finally transfer the contents of the dish to the filter-paper. Wash with cold water[5] until all the chlorides have been washed out. Test a

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[1] Solutions, owing to their lower vapour pressure, usually evaporate more slowly than water. P. Lesage, *Compt. rend.*, **115**, 473, 1893. For rapid evaporations see S. Wurzel, *Met. Chem. Eng.*, **12**, 430, 1914; W. Hempel, *Ber.*, **21**, 900, 1888; B. Freeman, *Chemist-Analyst*, **14**, 11, 1915; T. B. Aldrich, *Journ. Biol. Chem.*, **23**, 255, 1915. K. M. Timofeyuk (*Zavodskaya Lab.*, **3**, 19, 1933; P. N. Grigor'ev and P. I. Pozharskaya, *ib.*, **5**, 1443, 1936; V. Vepritzhaya, *ib.*, **4**, 1514, 1935; *Ogneuporui*, **4**, 284, 1936) adds a 1 per cent. solution of gelatin, albumen or casein, which coagulates the silicic acid and so saves time.

[2] A. V. Meyer's evaporating funnel, fig. 62, is suitable (*Ber.*, **16**, 3000, 1883). The evaporating funnel has been raised a little in the diagram.

[3] F. Kehrmann (*Zeit. anorg. Chem.*, **39**, 48, 1904) and B. Flurscheim (*ib.*, **39**, 106, 1904) refer to a loss of silica by evaporation with acids; but C. Freidheim and A. Pinagel (*ib.*, **45**, 410, 1905) show that the loss probably occurred during the (careless) filtration, not during the evaporation. K. F. Fohr (*Berg. Hutt. Ztg.*, **41**, 252, 1882; *Chem. News*, **46**, 40, 1882; W. Skey, *ib.*, **16**, 207, 1867; D. H. Browne, *Journ. Anal. App. Chem.*, **5**, 342, 1891; A. Vogel, *Neues Rept. Pharm.*, **18**, 157, 1869) has stated that some ferric chloride is lost during the evaporation or during the drying of the residue at 130°. If, however, residues containing ammonium chloride or aqua regia be so treated, there is, according to Talbot, an appreciable loss of iron, though S. Shinkai (*Journ. Soc. Chem. Ind.*, Japan, **29**, 303, 1926) recommends the addition of 3 to 4 grms. of ammonium chloride when the solution has been reduced to small volume in order to convert the silica hydrosol into hydrogel, and states that the process is applicable to silicates containing the oxides of aluminium, iron, calcium and magnesium.

[4] For the influence of the drying temperature on the final result, see page 154 *et seq.*

[5] Washing with hot water is inclined to precipitate basic chlorides of iron with the silica. Basic iron salts, for instance, are precipitated on boiling slightly acid solutions in the presence of much alkali salts (S. P. U. Pickering, *Journ. Chem. Soc.*, **37**, 807, 1880). In that case, the

drop of the filtrate with a drop of silver nitrate solution; if there be no turbidity the washing is complete.

Second Evaporation.—The filtrate is transferred to the same basin as was used in the first evaporation, and the solution evaporated to dryness and the residue baked in the oven as before. Digest in dilute hydrochloric acid; filter through a 7 cm. filter-paper and collect the filtrate in the same beaker as was used in the first filtration. Take special care to remove all particles of silica which may adhere to the basin by rubbing with a "policeman."[1] Wash with cold water as before. The filtrate should occupy 150 to 200 c.c.[2]

Ignition of the Silica.—The free edges of the filter-paper are folded down on the silica and both filter-papers, while still moist, are placed in a weighed
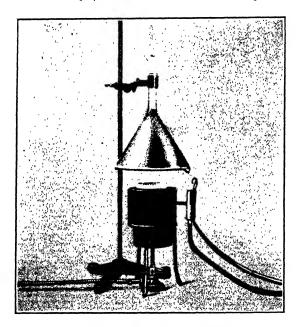
Fig. 62.—Evaporation for Silica.

platinum crucible. The paper containing the bulk of the silica is placed in the crucible first. The triple folds of the filter-paper are placed uppermost to facilitate oxidation. Heat the crucible and contents slowly over a Bunsen burner fitted with a mushroom head, until the paper is thoroughly charred,

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ignited silica is not white, but dirty brown. Cold water *is* therefore best for washing the silica of ferruginous clays, and this the more as sodium chloride is not much more soluble in hot water (39·8 grms. per 100 c.c. at 100°) than in cold water (35·9 grms. in 100 c.c. of water at 15°). But, other things being equal, hot solutions filter more rapidly than cold solutions.

[1] Dry the porcelain basin, when any traces of silica not transferred to the filter-paper can be easily detected as white spots (F. L. Kortright, *Chem. Eng.*, 5, 19, 1905). O. Knöfler (*Zeit. anal. Chem.*, 28, 673, 1889) recommends a dark underglaze colour in the interior of evaporating basins to show up any traces of residues or precipitates like aluminium hydroxide, etc. F. Moldenhauer (*Zeit. anal. Chem.*, 50, 754, 1911) recommends platinum basins. S. R. Scholes (*Chemist-Analyst*, 29, 22, 1920) adds a small amount of methyl orange before each evaporation; the dye stains the gelatinous solid as it separates and every particle becomes coloured.

[2] A trace of silica passes into the second filtrate, and is partly recovered at a later stage of the analysis, as "extra silica."

but at no stage allow the paper to ignite or there will be a danger of the escaping gases whirling the light powdered silica out of the crucible. Then remove the mushroom head and gradually burn off the carbonaceous residue, after which put the cover on the crucible, and blast the silica for 20 to 30 minutes in order to dehydrate it and render it less hygroscopic. Cool in a desiccator and weigh.[1] The silica should naturally be ignited until no further loss in weight occurs, but experience shows that the above period is ample with a good blast.[2] Record the weight as indicated below: "Uncorrected silica plus crucible."

Impurities in the Silica.—The silica so obtained is not quite pure. A more or less dark grey coloured silica results from the ignition of the *moist* precipitate in a *covered* crucible and is due apparently to the formation of silicon carbide, SiC.[3] It probably contains small quantities of titanic oxide, phosphoric oxide, alumina and ferric oxide.[4] Add 5 c.c. of water[5] and about 5 drops of concentrated sulphuric acid. The latter is necessary to prevent the volatilisation of titanium fluoride[6]—TiF_4 (and possibly also some aluminium fluoride—AlF_3). Add hydrofluoric acid[7] carefully, a few drops at a time, to prevent loss

[1] The lower the temperature at which the silica is calcined, the more hygroscopic the resulting powder. A. Souchay (*Zeit. anal. Chem.*, 8, 423, 1869) states that precipitated silica calcined at a low temperature adsorbed 14·38 grms. of hygroscopic moisture per 100 grms. of silica; silica calcined at the full temperature of a Bunsen burner, 2·00 grms. per 100 grms. of silica; and silica calcined in a blast, 0·09 grm. of hygroscopic moisture per 100 grms. of silica. Powdered quartz under similar conditions adsorbed no hygroscopic moisture—J. W. Mellor and A. D. Holdcroft, *Trans. Cer. Soc.*, 10, 94, 1911.

[2] This point should, however, be verified. See also T. Bauer (*Tonind. Ztg.*, 37, 89, 1913) for the difficulty in removing the last traces of hydrochloric acid.

[3] K. A. Krieger and H. S. Lukens, *Ind. Eng. Chem. Anal. Ed.*, 8, 118, 1936.

[4] And, in special cases, lead sulphate, calcium and barium sulphates, tin oxide, antimony oxide, tungsten oxide, and basic salts. Silica is very liable to retain phosphoric and tungstic acids—W. Skey, *Chem. News*, 16, 187, 1867; and also arsenic and tin oxides—if present.

[5] Be careful in adding liquids to dry powders (especially if hot). There is a tendency for some of the powder to be dissipated as a "cloud of dust"—E. Jordis and W. Ludewig, *Zeit. anorg. Chem.*, 47, 180, 1905.

[6] E. Riley, *Journ. Chem. Soc.*, 12, 13, 1860; P. Holland, *Chem. News*, 59, 27, 1889; P. Truchot, *Rev. gén. Chim.*, 18, 173, 1905. Thus, Holland has shown that titanic oxide is lost by fuming with hydrofluoric acid when sulphuric acid is absent, but not when it is present:

Sulphuric acid.	TiO_2 present.	TiO_2 found.
None present	0·0466	0·0340
Present	0·0414	0·0413
Present	0·0520	0·0520

E. Wedekind (*Ber.*, 44, 1753, 1911) has also shown that the presence of sulphuric acid considerably reduces the loss of zirconium when fuming with hydrofluoric acid to drive off the silica. S. B. Kuzirian, *Amer. Journ. Science*, (4), 37, 61, 1914; *Zeit. anorg. Chem.*, 85, 430, 1914.

[7] HYDROFLUORIC ACID.—The acid must be free from non-volatile impurities—K. F. Stahl, *Zeit. öffent. Chem.*, 3, 13, 1896; A. H. Allen, *Analyst*, 21, 87, 1896; B. Blount, *ib.*, 21, 87, 1896. Hydrofluosilicic acid, derived from the silica in the fluorspar used in the manufacture of the hydrofluoric acid, is a common impurity. Sulphuric acid, as well as hydrofluosilicic acid, may distil over with the hydrofluoric acid. The acid may also contain substances which reduce potassium permanganate (pages 178, 219 and 513). For apparatus for working with hydrofluoric acid, see G. Foord, *Chem. News*, 30, 191, 1874 (apparatus for pouring); E. Cohen, *Natur. Ver. Neuvorpommern Rugen*, 20, 1, 1889; H. C. Andersch, *Chem. Ztg.*, 12, 1475, 1888; R. Benedict, *ib.*, 15, 881, 1891; E. Hart, *Journ. Anal. App. Chem.*, 3, 372, 1889 (bottles for); G. P. Vanier, *ib.*, 4, 48, 1890 (pipette); R. Hamilton, *Chem. News*, 60, 252, 1889; W. Hempel, *Ber.*, 18, 1434, 1885; A. P. Stuart, *Amer. Chemist*, 2, 384, 1871 (preparation of pure acid); J. Zellner, *Monats.* 18, 749, 1897 (determining concentration). A drop of hydrofluoric acid on the skin produces a serious "burn." According to M. Kessler (*Chem. News*, 8, 17,

by the violent effervescence which sometimes occurs.   The crucible is filled not quite half-full with hydrofluoric acid.   Place the crucible *eccentrically* on a sand bath and slowly evaporate the solution almost to dryness.   Add 2 or 3 c.c. more hydrofluoric acid, and take the contents of the crucible to complete dryness on the sand bath.   After removing any grains of sand from the outside of the crucible heat it to bright redness and blast the residue five minutes.[1]   Weigh the crucible and contents, and enter the result as "crucible plus residue." The difference between this weight and the preceding represents the silica.[2] A minute quantity of silica has yet to be added to the silica so determined— the "extra silica" of page 167.

It is here assumed that the residue in the crucible is free from lime, magnesia and alkali salts, and that the crucible only contains constituents belonging to the ammonia precipitate.   Bloor[3] has investigated the validity of this assumption by analysing the residues.   He found among other determinations that:—

Table XXIV.— Composition of the Silica Residues.

Total residue.	Alumina.	Ferric oxide.	Magnesia.	Lime.
0·0072	0·0023	0·0008	0·0022	0·0007
0·0062	0·0006	0·0020	0·0014	0·0005
0·0080	0·0018	0·0020	0·0007	0·0020
0·0036	0·0000	0·0010	0·0014	0·0004
0·0074	0·0028	0·0018	0·0000	0·0020
0·0046	0·0006	0·0018	0·0000	0·0023
0·0080	0·0025	0·0031	0·0012	0·0008
0·0013	0·0000	0·0000	0·0005	0·0012

Hence, Bloor concludes that the residue "is contaminated to some degree by the main constituents of the clay.   The amount of contamination by substances other than ferric oxide and alumina is, however, except in extreme cases,[4] so small that it may be neglected unless extreme accuracy is required"; in that case the residue can be taken up with a little sodium carbonate, and the acid solution of the fused mass added to the main solution.

Weighings.—The results of the silica weighings in the above operations, together with the "extra silica" from a later operation, will be recorded somewhat as follows:—

1863), the "first aid" treatment for hydrofluoric acid on the skin is to use lint wetted with ammonium acetate and inject the same solution into the blisters.   If the acid has touched parts of the skin difficult to moisten, *e.g.* under the nails, concentrated ammonia will give the best results.   The excruciating pain which attends the first application of the ammonia is transient.

[1] It is important to drive off all the hydrofluoric acid, or troubles with the alumina will follow later.

[2] S. V. Peppel reports that the loss in weight obtained on treating the insoluble residue from low-grade limestones with hydrofluoric and sulphuric acids is sometimes greater than the amount of silica actually present—H. E. Ashley, *Chem. News*, 90, 274, 1904.   For the volatilisation of silica, see E. Cramer, *Zeit. angew. Chem.*, 5, 484, 1892; H. Moissan, *Compt. rend.*, 116, 1222, 1429, 1893; P. Schützenberger, *ib.*, 116, 1230, 1893; L. Troost, *ib.*, 116, 1428, 1893.

[3] W. R. Bloor, *Journ. Amer. Chem. Soc.*, 29, 1603, 1907; C. Meineke, *Rep. anal. Chem.*, 7, 214, 1887; E. Jordis, *Zeit. anorg. Chem.*, 45, 362, 1905. M. Aurousseau (*Journ. Washington Acad. Sciences*, 13, 330, 1923) found that 31·4 per cent. of the total titanic oxide in an andesite was retained in the silica residue.

[4] *E.g.* when the amount of magnesium or calcium in the original sample is high, as was the case with the third sample in the above table.

Crucible, silica and residue	.	.	.	.	.	.	21·0603 grms.
Crucible and residue [1]	.	.	.	.	.	.	20·4552 „
Crucible alone [2]	.	.	.	.	.	.	20·4530 „
Corrected silica	.	.	.	.	.	.	0·6051 grm.

Crucible, extra silica and residue	.	.	.	.	.	22·9531 grms.
Crucible and residue	.	.	.	.	.	.	22·9522 „
Extra silica	.	.	.	.	.	.	0·0009 grm.

Corrected silica	.	.	.	.	.	.	0·6051 grm.
Extra silica	.	.	.	.	.	.	0·0009 „
Silica found	.	.	.	.	.	.	0·6060 grm.
Less silica in reagents	.	.	.	.	.	0·0008 „
Total silica	.	.	.	.	.	.	0·6052 grm.

Errors.—The following results were obtained in eight independent determinations with one sample of clay:—0·6052; 0·6048; 0·6047; 0·6046; 0·6053; 0·6044; 0·6044; 0·6043 grm. The mean is 0·6047 grm., or 60·47 per cent., with a deviation of about ±0·05. The deviations will be different with clays containing different amounts of silica. But if this particular sample be analysed by another analyst, we should expect the silica to come somewhere between 60·42 and 60·52 per cent. The variations obtained with a number of analyses as indicated above give an idea of the errors liable to affect particular determinations, but they tell nothing about the presence or absence of constant errors—say, errors due to the solubility of silica in the mother liquid.[3] The case of lithium, page 604, might be cited as an instructive example. These constant errors can rarely be checked, although an approximate idea can sometimes be obtained by control analyses with artificial mixtures containing known amounts of the constituents under investigation—page 243.[4]

Every method of analysis has its own peculiar sources of error. The principal sources of error in silica determinations are: (1) Imperfect decomposition of the silicate; (2) Loss by spurting when the acid is added to the carbonate fusion; (3) Imperfect transfer of the silica from dish to filter-paper; (4) Tendency of silica to remain in a soluble condition after baking at 109°; (5) Mechanical loss of fine particles of silica transported with the gases during incineration of the filter-paper, and during the dehydration of the silica; (6) Contamination by the reagents, and by the porcelain vessel during evaporation; and (7) Loss of weight of the crucible itself during the prolonged blasting.[5]

Determination of Silica in the Presence of Fluorides.—If fluorine be present as, say, calcium fluoride, part of the silica will be lost by volatilisation as silicon

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[1] Analyses of twelve clays gave residues varying from 0·0050 grm. to 0·0240 grm. with an average of 0·0107 grm.

[2] The loss in weight by the blasting of the crucible was negligibly small for the small crucible employed. If the crucible lost appreciably in weight during the blasting, write: "Empty crucible plus loss in weight during blasting." See page 97.

[3] For a critical examination and discussion of errors in silicate analysis, see W. Mylius, *Glashütte*, **62**, 782, 1932.

[4] M. Stoermer (*Tonind. Ztg.*, **35**, 453, 1911) considers that alumina is volatilised when the silica is heated with sulphuric and hydrofluoric acids. No appreciable loss can be detected under the conditions of the experiment described in the text.

[5] For a discussion of methods in use for the determination of silica, see P. Grigor'ev, *Stroitelnuie Materialui*, No. 9, 1930; *Ceram. Abs.*, **10**, 384, 1931. For the volumetric determination of silica, see A. Travers, *Compt. rend.*, **173**, 174, 1921; N. A. Tananaev and A. K. Babko, *Ukrain. Khem. Zhur. Sci. Pt.*, **5**, 71, 1930; *Zeit. anal. Chem.*, **82**, 145, 1930.

tetrafluoride—SiF_4—when the solution is evaporated to dryness. Supposing, in the extreme case, that all the fluorine be so evolved, the maximum possible loss of silica will be nearly equal to three-eighths of the weight of the calcium fluoride. The error becomes appreciable in the case of Cornish stone, which contains from 2 to 5 per cent. of calcium fluoride. In this case the silica and fluorine must be separately determined, as indicated on page 731.

Determination of Silica in the Presence of Boric Oxide.—When borates are present, it is necessary to get rid of the boric oxide by adding methyl alcohol, saturated with hydrogen chloride, during the evaporation for silica, as indicated on page 664.

§ 78. The Theory of Silica Determinations.

When an aqueous solution of sodium silicate is treated with hydrochloric acid,[1] part of the silicate will be decomposed, forming sodium chloride and silicic acid, say, $H_{2n}SiO_{n+2}$. Conversely, when a solution of silicic acid is treated with sodium chloride, hydrochloric acid and sodium silicate are produced. These reactions are symbolised:

$$2n\text{NaCl} + n\text{H}_2\text{O.SiO}_2 \rightleftharpoons 2n\text{HCl} + n\text{Na}_2\text{O.SiO}_2$$

The reversed arrows represent the fact that the reaction proceeds in each direction. When the speeds of the two reactions are the same, the system is in equilibrium, and the solution contains all four substances in certain definite proportions. If not, the system is not in equilibrium, and it will tend to attain that condition. Whatever be the condition of the system after it has been evaporated to dryness, when the residue is taken up with dilute acid, a definite proportion of the silica in solution will be present as colloidal silicic acid,[2] and the rest as sodium silicate.

If all the soluble silicic acid in the dried residue could be converted into insoluble silicic acid by baking at a high temperature, the sodium silicate, when taken up with more hydrochloric acid, would be hydrolysed and furnish the same relative proportions of soluble silicic acid and sodium silicate as before. If the silicic acid so formed could be rendered insoluble by another evaporation, it follows that repeated evaporation to dryness and soaking the dried residue would transform practically all the silica into the insoluble condition, and the filtrate would be practically free from silica. Some analysts are under the impression that the action does occur, and recommend this procedure.[3]

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[1] Gelatinous orthosilicic acid—H_4SiO_4—is precipitated. This, when heated, or digested with sulphuric acid, forms metasilicic acid—H_2SiO_3 (R. Meldrum, *Chem. News*, 78, 235, 1898); and this at 100°–110° forms the trisilicic acid—$H_2Si_3O_7$—which is insoluble in water and acids: at a high temperature the latter is converted into anhydrous silica.

[2] For the solubility of silica, see R. Bunsen, *Pogg. Ann.*, 61, 265, 1847; E. Ludwig, *Zeit. anal. Chem.*, 9, 321, 1870; C. Meineke, *Rep. anal. Chem.*, 7, 214, 757, 1887; P. Jannasch and O. Heidenreich, *Zeit. anorg. Chem.*, 12, 214, 1896; C. Winkler, *Chem. Centr.*, 4, 673, 1859; J. W. Mellor and A. D. Holdcroft, *Trans. Cer. Soc.*, 10, 1, 1911; A. M. Edwards, *Chem. News*, 73, 13, 1896; V. Lenher and E. Truog, *Journ. Amer. Chem. Soc.*, 38, 1050, 1916; V. Lenher and H. B. Merrill, *ib.*, 39, 2630, 1917; F. G. Hawley, *Eng. Min. Journ.*, 103, 541, 1917; M. Wunder and A. Suleimann (*Ann. Chim. anal.*, 19, 45, 1914) found that the solubility of precipitated silica increases with the strength of the acid used and the temperature of digestion. For the alleged relatively greater solubility of silica in hydrochloric acid than in aqua regia, see G. C. Wittstein, *Zeit. anal. Chem.*, 7, 433, 1868. For the solubility of silica in alcohol saturated with hydrogen chloride, see W. Knop, *Répertm. Chim. appl.*, 1, 71, 1859; A. Winkler, *Chem. Centr.*, 4, 673, 1859. For the solubility of silica in aq. ammonia, see page 165.

[3] *E.g.* G. Lunge, *Technical Methods of Chemical Analysis*, London, 1, 581, 1908. M. Stoermer (*Tonind. Ztg.*, 35, 453, 1911) considers that all the silica is converted into an insoluble form by evaporating the hydrochloric acid solution, baking at 130° and soaking two hours

The percentage amount of water lost per hour in the earlier stages of the drying (110°) is very much greater than in the later stages. Indeed, the last stage of the dehydration requires an indefinitely long time for its completion.[1] This is illustrated by the gradual approach of the curve (silicic acid containing 23·9 per cent. water), fig. 63, to a horizontal line. If the temperature be
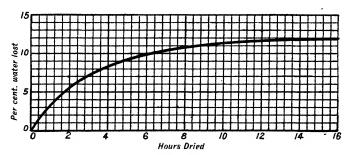
FIG. 63.—Effect of Time occupied by Drying at 110° on the Dehydration of Silicic Acid.

raised, the transformation takes place much more rapidly and completely; but experience shows that the higher the desiccation temperature, the greater the amount of foreign matter associated with the silica. "This," says Gilbert,[2] "is probably due to the alumina being rendered insoluble in acids." See Table XXV.

If the amount of alumina be high, the residue left after the removal of silica is greater the higher the drying temperature. In the case of calcareous slags (46 per cent. CaO), the calcium chloride in the residue seems to facilitate the dehydration of the silica and reduce the amount of silica soluble in the filtrate. On the other hand, with a slag containing 35 per cent. of CaO and 15 per cent. of MgO, the magnesium chloride seems to retard the dehydration at 100°; and at 280° it increases the amount of soluble silica in the filtrate.

Hillebrand[3] considers that magnesia begins to recombine with silica to form a magnesium silicate at temperatures over 120°. This silicate is subsequently decomposed by hydrochloric acid, with the separation of silica. It is not, therefore, possible to separate all the silica by the evaporation of magnesian clays if the residue be dried at temperatures over 120°. A certain amount of soluble silica will always be formed by the decomposition of the resulting magnesium silicate. If magnesium be absent, the drying of calcareous silicates can be conducted at a higher temperature than 110°—for instance, 280°—when "it would seem that there is no tendency for silica to recombine with lime and alumina" (Gilbert).[4]

with hydrochloric acid. He considers a second evaporation to be unnecessary, for it makes no difference whether or not the silica be filtered off before the second evaporation. The experimental results quoted in this chapter show that two evaporations with an intervening filtration are necessary for exact work; but see the section on abbreviated systems of analysis, page 239.

[1] J. M. van Bemmelen, *Zeit. anorg. Chem.*, **13**, 233, 1897; *Die Adsorption*, Dresden, 196, 1910. According to P. H. Walker and J. B. Wilson (*Circ. U.S. Dept. Agric.*, **101**, 1, 1912), a two-hours' ignition at the highest temperature obtainable with a Bunsen burner suffices for the dehydration of silica, and three hours for alumina; there is then no risk of error owing to a change in weight of the platinum crucible.

[2] J. P. Gilbert, *Tech. Quart.*, **3**, 61, 1890; *Chem. News*, **61**, 270, 281, 1890; G. Craig, *ib.*, **60**, 227, 1889; W. J. Rees, *Journ. Soc. Glass Tech.*, **11**, 172, 1927.

[3] W. F. Hillebrand, *Journ. Amer. Chem. Soc.*, **24**, 262, 1904.

[4] If zinc be present, see page 379.

*Table XXV.—Effect of the Dehydration Temperature on the
Determination of Silica in Clays.*

1. Aluminous Clays.				
Total SiO₂ per cent.	Temperature.	Residue after first evaporation (per cent.).	Residue after second evaporation (per cent.).	SiO₂ in filtrate (per cent.).
64·15	100°	64·46	0·0018	0·0017
64·28	120°	64·19	0·0023	0·0032
64·55	280°	64·90	0·0070	0·0035
2. Calcareous Clays.				
41·28	100°	41·33	0·0013	0·0008
41·20	120°	41·32	0·0018	0·0006
41·52	280°	41·78	0·0029	0·0003
3. Magnesian Clays.				
33·70	100°	33·67	0·0020	0·0023
33·80	120°	33·63	0·0028	0·0008
33·94	280°	33·81	0·0065	0·0052

So long as any silica escapes transformation into the insoluble condition, so long will a certain proportion pass into solution probably as sodium silicate, by the reaction between the sodium chloride and silicic acid. In illustration, A. B. Trickett mixed pure silicic acid with different proportions of 20 per cent. sodium chloride solution, evaporated the mixture to dryness and baked the residue four hours in a steam oven. The insoluble silica was filtered off, washed and the soluble silica determined in the filtrate by the molybdate colorimetric process (page 686).

Table XXVI.—Effect of Sodium Chloride on "Soluble" Silica.

Grms. NaCl per grm. SiO₂.	SiO₂ in the filtrate (per cent.).
18·5	0·78
26·9	0·81
45·8	1·06
62·4	1·07

This shows that the greater the amount of sodium chloride in the solution, the greater the amount of silica in the filtrate, presumably owing to the transformation of silicic acid into soluble sodium silicate.

This re-solution of sodium silicate is one of the troubles attending the determination of silica. If the silicic acids could be completely dehydrated by baking below the temperature of recombination, the difficulty would be overcome. It is important to remove as much silica as possible at this stage of the

analysis, since any silica which escapes in the filtrate will contaminate the different precipitates later on.[1]   The possibility of a *recombination of the silica with the bases during the baking of the silica limits the safe temperature of desiccation*.[2]   The complete drying, that is, the complete conversion of the silica into the insoluble form, might possibly be effected at 110° if an indefinite period of time were available.   The longer the time of baking, the more perfect the drying, and the less the amount of silica which passes into solution in the filtrate.   This is illustrated by the following experiments due to Hillebrand:—

Table XXVII.—Effect of Time of Drying on the "Soluble" Silica.

Hours of drying in steam oven	4	24	48
Per cent. of silica in filtrate	2·11	1·63	1·48

In agreement with fig. 63, it follows that the complete "dehydration" of the silicic acid is excessively slow—too slow to be of any practical use.[3]   It will therefore be obvious that taking up the dry residue with hydrochloric acid and re-drying the residue a number of times has very little influence on the "silica in filtrate."   But if the silica which has separated be removed, the amount of silica remaining when the filtrate is evaporated to dryness is comparatively small.   The drying curve for this silica resembles that indicated in fig. 63; and although a similar percentage of the silica will remain untransformed at the end of a certain period of drying, yet the actual amount is small in comparison with the total silica.   Indeed, after the second evaporation and drying, less than 0·1 per cent. of the total silica will be found in the filtrate.   This is very well illustrated by the two following sets of numbers which show the amounts of silica remaining in the filtrates after successive evaporations and bakings:—

Filtrate.	First.	Second.	Third.	Fourth.
Silica	0·00141	0·00081	0·00023	0·00006 grm.
Silica	0·0307	0·0035	0·0024	0·0015 grm.

Cameron recommends the third evaporation, thus reducing the percentage silica in the third filtrate to a negligibly small amount, and after the fourth evaporation, the amount escaping dehydration is almost out of range of the balance.[4]   Two evaporations suffice for technical work.

It follows from Table XXV., section 2, that when the silicate under investigation is soluble, or almost wholly soluble, in acid, say hydrochloric acid,

[1] R. Bunsen, *Liebig's Ann.*, **61**, 265, 1847; E. Ludwig, *Pogg. Ann.*, **141**, 149, 1870; *Zeit. anal. Chem.*, **9**, 321, 1870; C. Meineke, *Rep. anal. Chem.*, **7**, 214, 1887; A. Cameron, *Chem. News*, **69**, 171, 1894; E. Jordis and W. Ludewig, *Zeit. anorg. Chem.*, **45**, 362, 1905; **47**, 180, 1905; N. Knight and F. A. Menneke, *Chem. News*, **94**, 165, 1906; J. A. Phillips, *Phil. Mag.*, (4), **41**, 87, 1871; F. A. Gooch, F. C. Reckert and S. B. Kuzirian, *Amer. Journ. Science*, (4), **36**, 598, 1913; *Zeit. anorg. Chem.*, **85**, 230, 1914; P. Nicolardot and J. Koenig, *Ann. Chim. anal.*, **23**, 104, 1918; V. Lenher and E. Truog, *Journ. Amer. Chem. Soc.*, **38**, 1050, 1916.

[2] B. Blount, *Journ. Amer. Chem. Soc.*, **26**, 995, 1904.   W. H. Stanger and B. Blount (*Journ. Soc. Chem. Ind.*, **21**, 1216, 1902) consider the temperature of baking Portland cements should not be lower than 200°.   This high temperature is not safe for general work, although with calcareous cements, under industrial conditions, the results are satisfactory (Table XXV.). T. Bauer, *Tonind. Ztg.*, **37**, 89, 1913.

[3] It is probable that some volatile reagent—say alcohol—might be found to do the work efficiently, but this has not yet been fully investigated.

[4] In these experiments the residues were not baked above 110°.

and, in consequence, comparatively little sodium salt is present, one evaporation will be almost as effective as two. This explains how some discordant statements are rife. For instance, with Portland cement, which is nearly all soluble in hydrochloric acid, one evaporation and baking at 180° will suffice. The relatively large proportion of lime in these silicates also facilitates the dehydration of the silica, as indicated in the same section of Table XXV.[1]

Evaporation with sulphuric acid,[2] in place of hydrochloric acid, gives a silica which is comparatively easily dehydrated;[3] but the presence of this acid is a source of danger on account of the risk of forming sparingly soluble sulphates which may contaminate the silica, and the escape of alumina from precipitation in the presence of sulphates—page 161. Evaporation with perchloric acid has already been mentioned.[4]

The rate at which the silicic acid is dehydrated is connected with the concentration of the solution from which the silicic acid was precipitated by the hydrochloric acid. For instance, J. C. Green has measured the rate of expulsion of water at 800° from silicic acid precipitated from concentrated and from dilute solutions of sodium silicate, and afterwards dried by heating up to 450°. His results are:—

Table XXVIII.—Dehydration of Silicic Acid at 800°.

Time heated at 800°. Minutes.	Amount of moisture lost—per cent.	
	Silica from concentrated solutions.	Silica from dilute solutions.
5	1·6	4·49
10	4·25	6·45
20	5·72	8·72
30	6·18	10·04

According to Gooch,[5] the difficulty in igniting silica to constant weight is not due to the retention of water, but to the presence of some substance slowly decomposed or volatilised by heat—usually sodium chloride, sometimes sulphate.

[1] B. Blount, *Journ. Amer. Chem. Soc.*, **26**, 995, 1904; S. F. Peckham, *ib.*, **26**, 1636, 1904.

[2] T. N. Drown, *Chem. News*, **40**, 40, 1879; **42**, 331, 1880; *Trans. Amer. Inst. Min. Eng.*, **7**, 346, 1879; T. N. Drown and P. W. Shimer, *ib.*, **8**, 508, 1880; J. Thill, *Zeit. anal. Chem.*, **43**, 552, 1904; G. H. Meeker, *Journ. Amer. Chem. Soc.*, **19**, 370, 1897; A. Cameron, *Chem. News*, **69**, 674, 1894; C. Craig, *ib.*, **60**, 227, 1889; J. P. Gilbert, *ib.*, **61**, 270, 281, 1890; V. Lehner and E. Truog, *Journ. Amer. Chem. Soc.*, **38**, 1050, 1916; F. G. Hawley, *Eng. Min. Journ.*, **103**, 541, 1917; H. A. B. Motherwell, *ib.*, **103**, 1155, 1917. V. M. Goldschmidt (*Tids. Kemie Pharm. Terap.*, 325, 1910) recommends making the silica insoluble by evaporation with nitric acid and hydrogen peroxide instead of with hydrochloric acid.

[3] Nitric acid is used in special cases—for instance, when lead is present.

[4] See footnote 4, page 145.

[5] F. A. Gooch, F. C. Reckert and S. B. Kuzirian, *Amer. Journ. Science*, (4), **36**, 598, 1913; *Zeit. anorg. Chem.*, **85**, 230, 1914; S. B. Kuzirian, *Amer. Journ. Science*, (4), **37**, 61, 1914; *Zeit. anorg. Chem.*, **85**, 430, 1914.

CHAPTER XIII.

THE AMMONIA PRECIPITATE.

§ 79. The Precipitation by Means of Ammonia.

WE have now to deal with the filtrate, acidified with hydrochloric acid, from the silica. This solution contains aluminium, iron, titanium, phosphorus, manganese, calcium, magnesium and alkali salts.[1] Assume that the manganese is either absent, or present in inappreciable quantities.[2] The addition of ammonia, in the presence of ammonium chloride,[3] precipitates the aluminium, iron,[4] phosphorus, titanium[5] and part of the magnesium. The precipitate carries down a little lime and alkalies.[6] Two to three grams of solid ammonium chloride are added to the solution and then a slight excess of ammonia is added drop by drop with constant stirring. "If an excess of ammonia be poured into the solution rather quickly, a considerable quantity

[1] If lead, bismuth, copper, cadmium, tin, arsenic, molybdenum, antimony, selenium, gold and the platinum metals be present, they should be removed by hydrogen sulphide, as indicated later on page 168.

[2] If manganese be present, and time is of great importance, add a few cubic centimetres of bromine water (page 393) to the boiling solution containing the equivalent of 10 per cent. of concentrated hydrochloric acid by volume and make the solution alkaline with ammonia. Alternatively add "reagent" hydrogen peroxide with the ammonium chloride and ammonia— M. Dittrich, *Ber.*, 35, 4072, 1902. The manganese will be precipitated with the alumina and iron. The presence of one part of iron in 80,000 parts of solution gives a visible precipitate with aqueous ammonia; for aluminium the numbers are 1 : 100,000; for chromium, 1 : 170,000; zinc, 1 : 80,000; manganese, 1 : 170,000—L. J. Curtmann and A. D. St John, *Journ. Amer. Chem. Soc.*, 34, 1679, 1912.

[3] A. Mitscherlich, *Journ. prakt. Chem.*, (1), 81, 108, 1860; (1), 83, 458, 1861.

[4] Ferric, not ferrous, hydroxide. But the iron after the preceding treatment will generally be all in the ferric state. If much manganese be present (as will be indicated by the colour of the sodium carbonate fusion), the filtrate from the silica may contain ferrous iron. "The tendency of manganese salts to exert a reducing effect on ferric iron in solution is probably the cause of this phenomenon"—G. C. Stone (W. G. Waring, *Journ. Amer. Chem. Soc.*, 26, 4, 1904). If ferrous salts be present, a few drops of "reagent" hydrogen peroxide will effect the conversion (A. Carnot, *Compt. rend.*, 107, 948, 997, 1888). If hydrogen sulphide has been used to remove the metals indicated in footnote 1, it will be necessary to remove the hydrogen sulphide by boiling, filter off the sulphur, if any, and oxidise the iron. Note that commercial hydrogen peroxide sometimes contains fluorine, chlorine, sulphuric acid, hydrofluosilicic acid, sugar, glycerine, calcium, magnesium, barium and aluminium salts—H. P. Talbot and H. R. Moody, *Tech. Quart.*, 5, 123, 1893; G. Arth, *Monit. Scient.*, (4), 15, 715, 1901; *Chem. News*, 85, 184, 1902.

[5] If chromium, beryllium, vanadium and the rare earths be present, they too will be precipitated as hydroxides; uranium will be precipitated as ammonium diuranate—$(NH_4)_2U_2O_7$.

[6] C. F. Cross, *Proc. Manchester Lit. Phil. Soc.*, 17, 49, 1877; P. Cornette, *Ann. Pharm.*, 4, 1, 1900; J. Thoulet, *Compt. rend.*, 99, 1072, 1884; R. Warrington, *Journ. Chem. Soc.*, 21, 1, 1868. Some consider that the precipitated hydroxide forms a true chemical compound with the substances in question. *E.g.* A. V. E. Young, *Amer. Chem. Journ.*, 8, 23, 1886 (Al); V. J. Hall, *ib.*, 19, 512, 1897 (Fe); 19, 901, 1897 (Zn); H. P. Patten, *ib.*, 18, 608, 1896 (Cr); *Journ. Amer. Chem. Soc.*, 25, 186, 1903 (Mg, Mn, $BaSO_4$).

of magnesia will be precipitated with the alumina"; whereas, "if the ammonia be added, drop by drop, with constant stirring, to the hot solution, until the ammonia is in slight excess, the precipitated alumina will be either free from magnesia, or retain but slight traces of that element." [1] In illustration, a mixture of 1·23 grms. of magnesium sulphate, with 2·2675 grms. of ammonia alum and 10 grms. of ammonium chloride in 750 c.c. of boiling water, gave precipitates which weighed, after ignition, 0·2581 grm. and 0·2641 grm., respectively, according to whether the precipitation was slow or rapid, whereas the calculated weight of the precipitate was 0·2560 grm. The precipitate is dissolved in hot hydrochloric acid and reprecipitated, washed, ignited and weighed. The ignited mass is then fused with potassium bisulphate, and the resulting cake digested with water. The insoluble silica [2] is filtered off, washed and weighed as "extra silica." The iron, titanium, phosphorus and manganese, if present in the filtrate, are determined separately. Arsenious oxide is very tenaciously adsorbed by ferric hydroxide.[3] The amounts of these constituents are added together, and the difference between the sum and the weight of the total ammonia precipitate is the alumina. Before taking up details of the process, a few special points may be considered.

Ammonia for the "Alumina" Precipitation.—The ammonia used should be free from carbonates; otherwise, calcium carbonate will be precipitated with the alumina.[4] Ammonia [5] absorbs carbon dioxide from the atmosphere, and hence some analysts make a fresh solution of ammonia periodically for this work. If calcium carbonate be formed, H. Rose [6] thinks that it will be decomposed by the ammonium salts present in the solution, when the mixture is boiled. The ammonia should be kept preferably in ceresine bottles, or glass bottles lined on the inside with ceresine. Freshly prepared ammonia kept in common glass bottles for one month gave a residue of 0·7 mgrm. per 25 c.c.; in a Jena glass bottle, 0·4 mgrm.; and in ceresine bottles, no residue.[7]

The Solubility of Aluminium Hydroxide in Ammonia Solutions.—Aluminium hydroxide is appreciably soluble in aqueous ammonia and, according to Archibald and Habasian,[8] the solubility at 20° expressed in grams of

[1] L. F. J. Wrinkle, *Chem. News*, **22**, 4, 1870; H. Abich, *Pogg. Ann.*, **23**, 352, 1831; W. R. Nichols, *Amer. J. Science*, (2), **47**, 16, 1869. E. H. Swift and R. C. Barton (*Journ. Amer. Chem. Soc.*, **54**, 2219, 1932) recommend adding ammonia until the solution is basic to methyl red.

[2] The trace which escapes in the second filtrate mentioned in the preceding chapter, as well as any dissolved from the glass vessels and reagents will be, for the most part, recovered later.

[3] G. Lockemann and F. Lucius, *Zeit. phys. Chem.*, **83**, 735, 1913; G. Lockemann and M. Paucke, *Zeit. Kolloid. Chem.*, **8**, 273, 1911.

[4] For the action of ammonia on silica, see pages 152 and 165.

[5] The ammonia is tested for carbon dioxide by an aqueous solution of calcium chloride. There should be no opalescence. For the analysis of commercial "aqua ammonia," see J. D. Pennock and D. A. Morton, *Journ. Amer. Chem. Soc.*, **24**, 377, 1902. For pyridine in ammonia, see H. Ost, *Journ. prakt. Chem.*, (2), **28**, 271, 1883; for lead, see W. F. Lowe, *Journ. Soc. Chem. Ind.*, **11**, 133, 1892. The latter impurity is introduced when the manufacturer places the ammonia in leaden vessels for dilution to the required specific gravity. C. Kollo and N. Georgian (*Bul. Soc. chim. Romănia*, **6**, 111, 1924) use hexamethylenetetramine, which readily hydrolyses in water to ammonium hydroxide and formaldehyde, instead of ammonia, one gram of the crystalline reagent being taken for each precipitation. B. Solaja (*Chem. Ztg.*, **49**, 337, 1925) recommends "infusible white precipitate" ($HgNH_2Cl$) for the precipitation of aluminium and iron hydroxides, separation from manganese being effected by one precipitation. For the precipitation of aluminium (as basic succinate) by urea, see H. H. Willard and N. K. Tang, *Ind. Eng. Chem. Anal. Ed.*, **9**, 357, 1937.

[6] H. Rose, *Chem. News*, **2**, 291, 1860; *Pogg. Ann.*, **110**, 292, 1860.

[7] E. T. Allen and J. Johnston, *Journ. Ind. Eng. Chem.*, **2**, 196, 1910.

[8] E. H. Archibald and Y. Habasian, *Trans. Roy. Soc. Canada*, **10**, 69, 1916.

aluminium hydroxide per 100 c.c. of solution varies with the normality of the ammonium hydroxide solution as follows:—

Normality	0·050	0·100	0·125	0·200	0·500	1·000
Solubility	0·007	0·008	0·025	0·038	0·045	0·024

The presence of ammonium nitrate decreases the solubility: thus, with a normal solution of ammonia at 20° and with p per cent. by weight of ammonium nitrate, the corresponding solubilities are:—

p	0	5	10	20	30
Solubility	0·024	0·0187	0·0082	0·0045	0·0035

On the other hand, potassium nitrate increases the solubility. Blum[1] says that complete precipitation occurs at p_H 6·5 to 7·5. Hence, before precipitation he adds a few drops of a 0·2 per cent. alcoholic solution of phenol red, followed by ammonia until the colour turns red.

Influence of Boiling and Long Standing on the Alumina Precipitate.—There are some objections to boiling solutions containing the alumina precipitate. Rose and Fresenius[2] recommend boiling off the excess of ammonia from the solution. Lunge[3] considers the boiling unnecessary. The objections to the boiling are: (1) Some alumina may be redissolved by prolonged boiling owing to the decomposition of the ammonium chloride, with the formation of hydrochloric acid and volatile ammonia.[4] Hence, it is well to make sure that the solution is alkaline before filtering. (2) Prolonged boiling to drive off the excess of ammonia may lead to a contamination of the precipitate by dissolution of silica from the glass vessels.[5] (3) Prolonged boiling also tends to make the precipitate slimy and difficult to filter and wash. The same objection applies to precipitates which have stood some time. (4) Calcium carbonate is also precipitated under these conditions owing to the absorption of carbon dioxide from the air.

The important thing is to filter and wash rapidly. If these operations for the precipitate from a gram of clay occupy much over half an hour, it will be almost impossible to remove the adsorbed salts, in a reasonable time, by the washing—hence some use a hot funnel (fig. 90). If the precipitate has reached the slimy stage[6] before the washing is completed, it is generally advisable to

[1] W. Blum, *Journ. Amer. Chem. Soc.*, 38, 1282, 1916.

[2] R. Fresenius, *Anleitung zur quantitativen chemischen Analyse*, Braunschweig, 1, 160, 1903; London, 1, 192, 1900; L. Blum, *Zeit. anal. Chem.*, 27, 19, 1888; H. Rose, *l.c.*; J. Löwe, *Zeit. anal. Chem.*, 4, 359, 1865. For the action of ammonium chloride on metallic sulphides, see P. de Clermont, *Compt. rend.*, 88, 972, 1879.

[3] G. Lunge, *Zeit. angew. Chem.*, 2, 635, 1889; G. Lunge and H. von Kéler, *ib.*, 7, 670, 1894; C. Meineke, *Rep. anal. Chem.*, 7, 214, 757, 1887.

[4] R. Fresenius, *Anleitung zur quantitativen chemischen Analyse*, Braunschweig, 2, 807, 1905; R. Fittig, *Zeit. anal. Chem.*, 27, 29, 1888; *Liebig's Ann.*, 128, 189, 1863; H. C. Dibbits, *Zeit. anal. Chem.*, 15, 245, 1876; *Ber.*, 5, 820, 1872; A. R. Leeds, *Chem. News*, 29, 256, 1874; D. Gernez, *Compt. rend.*, 64, 606, 1867; H. von Helmont, *Zeit. anorg. Chem.*, 3, 115, 1892; C. F. Sidener and E. Pettijohn, *Journ. Ind. Eng. Chem.*, 8, 714, 1916; W. H. Withey, *Journ. Inst. Metals*, 15, 207, 1916.

[5] For the action of ammonium sulphate on glass, see M. Lachaud and C. Lepierre, *Bull. Soc. chim.*, (3), 7, 603, 1892.

[6] The precipitated aluminium and ferric hydroxides sometimes appear to dissolve and pass through the filter-paper, particularly towards the end of a washing—C. F. Cross, *Chem. News*, 39, 161, 1879; E. Schirm, *Collegium*, 99, 1911. G. P. Baxter and R. A. Hubbard (*Journ. Amer. Chem. Soc.*, 28, 1208, 1906) state "that the solubility of ferric oxide in ammonia is caused by the presence of some organic impurity in the ammonia," and they tried, without success, to reproduce the phenomenon by mixing methyl-, ethyl-, diethyl-, isoamyl-amines, ethylenediamine, aniline and phenylhydrazine with the ammonia. We have always attributed the phenomenon to a deflocculation of the colloidal precipitate (page 85). See also p. 165, footnote 4.

redissolve it in hydrochloric acid and reprecipitate. For the reasons stated above, in no circumstances must the alumina precipitate be allowed to stand in its mother liquor unfiltered.

Filtration of Gelatinous Precipitates. Before adding the ammonia, Dittrich [1] mixes the solution with macerated filter-paper pulp.[2] This facilitates the washing of the gelatinous precipitate, and also the oxidation of the precipitate during the ignition. The process gives good results. The precipitate is rather bulky, and accordingly a larger filter-paper must be used, and also a larger crucible for the ignition. A certain amount of salt is adsorbed by the filter-paper, although Mansier [3] says that sodium chloride is not retained by the washed paper. Do not use paper pulp for highly ferruginous clays, for reasons which will appear later (page 166).

In order to coagulate gelatinous precipitates and make them easy to filter, Divine [4] recommends the addition of 6 c.c. of a 2·5 per cent. solution of tannin— the addition of 2 c.c. of the tannin solution, before adding the ammonia, works well. Guyard [5] recommended the addition of glycerol; Palmer, stirring with one or two drops of albumen (white of egg), and heating to boiling; Liebermann uses starch in a similar manner; Warren, a few drops of an ethereal solution of pyroxylin; and Zulkowsky recommended shaking the liquid with one-third of its volume of ether. The ether entangles the precipitate and carries it to the surface. Some of these recommendations must be adopted with caution, on account of the tendency of organic substances to retard the precipitation of alumina (see page 384). Glycerol, for instance, is under certain conditions highly objectionable.[6]

Influence of Fluorides on the Precipitation of Alumina.—In the presence of fluorides the precipitation of aluminium hydroxide by ammonia is incomplete,[7] and this the more so, says Cavaignac,[8] in hot solutions than in the cold. It has also been stated that some aluminium may be lost by volatilisation as

[1] H. Jervis, *Chem. News*, 78, 257, 1898; F. Ibbotson, *Technics*, 2, 357, 1904; M. Dittrich, *Ber.*, 37, 1840, 1904. C. F. McKenna (*Journ. Amer. Soc.*, 21, 125, 1899; *Chem. News*, 79, 184, 1899) recommended the paper pulp process for zinc sulphide in 1899; E. Murmann (*Zeit. anal. Chem.*, 50, 742, 1911) recommends the addition of a little of the finest starch, mercuric sulphide or shredded paper for gelatinous precipitates like aluminium hydroxide, manganese and zinc sulphides.

[2] PAPER PULP FOR FILTRATION.—The pulp may be prepared for filtration in the following manner:—Crush Swedish filter-paper into small balls, put the balls into a large empty ceresine bottle. Add concentrated hydrochloric acid, and a little hydrofluoric acid. Seal up the stopper of the bottle with wax, and shake in a shaking machine for a couple of hours. Wash the resulting pulp free from acid by decantation. Keep the emulsion of pulp and water in a bottle for use.

[3] M. Mansier, *Rev. Internat. Falsif.*, 15, 115, 1903.

[4] R. E. Divine, *Journ. Soc. Chem. Ind.*, 24, 11, 1905.

[5] A. Guyard, *Zeit. anal. Chem.*, 22, 426, 1883; L. Liebermann, *ib.*, 14, 359, 1875; K. Zulkowsky, *Chem. Ztg.*, 8, 772, 1885; H. N. Warren, *Chem. News*, 61, 63, 1890; C. S. Palmer, *Eng. Min. Journ.*, 80, 582, 1906. T. M. Chatard (*Amer. J. Science*, (2), 50, 247, 1870; (3), 2, 416, 1871; *Chem. News*, 22, 246, 1870; 24, 270, 1871) recommends the evaporation of gelatinous precipitates to dryness on a water bath, when it is claimed that chromic, ferric, aluminium, beryllium and titanium hydroxides, nickel carbonate, cerium, lanthanum and didymium oxalates become granular and easy to filter. The washing of these precipitates free from salts is then a difficulty. F. L. Hahn (*Ber.*, 65B, 64, 1932) says that aluminium, iron and chromium hydroxides are precipitated from neutral solution in a dense, easily filtered form by using a mixture of sodium nitrite and sodium azide, NaN_3, as precipitant.

[6] A. Guyard, *Bull. Soc. chim.*, (2), 31, 354, 1879.

[7] F. P. Veitch, *Journ. Amer. Chem. Soc.*, 22, 246, 1900; W. R. Bloor, *ib.*, 29, 1603, 1907; L. J. Curtman and H. Dubin, *ib.*, 34, 1485, 1912; F. W. Hinrichsen, *Ber.*, 40, 1497, 1907; *Zeit. anorg. Chem.*, 58, 83, 1908.

[8] H. Cavaignac, *Compt. rend.*, 158, 948, 1914.

fluoride but, according to Selch,[1] this is not correct. A soluble aluminium fluoride is produced which is not completely decomposed by the ammonia. The reaction is represented by the equation:

$$AlF_3 + 3NH_4OH \rightleftharpoons Al(OH)_3 + 3NH_4F$$

The reaction therefore proceeds in both directions, and in all probability a soluble salt, $(NH_4)_3AlF_6$, is produced when much ammonium fluoride is present. The amount of alumina which remains in solution with increasing proportions of ammonium fluoride is shown in the graph, fig. 64, after Hinrichsen.
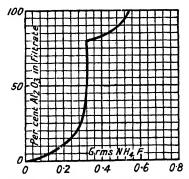
FIG. 64.— Action of Fluorides on the Precipitation of Alumina (Hinrichsen).
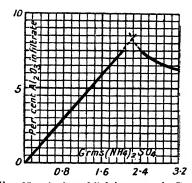
FIG. 65.—Action of Sulphates on the Precipitation of Alumina (Trickett).

Hinrichsen further showed the danger of introducing fluorine into the solution when clays and similar substances are opened up with sulphuric and hydrofluoric acids, and when the silica is corrected by treatment with the same acids, because of the difficulty in driving off the last traces of the fluorine. In these cases the solution should be evaporated to dryness, and the residue calcined in order to transform the fluorides into oxides. There is then no difficulty with the fluorine. It is well, however, to remember the difficulty in eliminating hydrofluoric acid from alumina even after repeated evaporation with sulphuric acid.[2]

Influence of Sulphates on the Precipitation of Alumina.—There is also a risk of alumina escaping precipitation in the presence of sulphates. A. B. Trickett, in our laboratory, has determined the amount of alumina which escapes precipitation in the presence of different amounts of ammonium sulphate, and his results are illustrated by the graph, fig. 65. Starting with the equivalent of 0·0077 grm. of alumina in solution, and increasing the amount of ammonium sulphate from 0·8 to 3·2 grms. (abscissæ, fig. 65), the corresponding amounts of alumina in solution when an excess of ammonia is added are represented in the diagram. The presence of a large excess of ammonium chloride appears to reduce the amount of alumina which escapes precipitation in this manner.

According to Wrinkle,[3] magnesia is much more liable to be precipitated with the alumina if sulphates be present.

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[1] E. Selch, *Zeit. anal. Chem.*, 54, 395, 1915.
[2] H. Cavaignac, *Compt. rend.*, 158, 948, 1914.
[3] L. F. J. Wrinkle, *Chem. News*, 22, 4, 1870. According to H. Bley (*Journ. prakt. Chem.*, (1), 39, 1, 1846), a certain amount of sulphuric acid or sulphate may also be dragged down with the precipitate.

§ 80. The Theory of the Ammonia Precipitation.

Les méthodes employées pour le dosage et la séparation des éléments Fe, Al, Cr, Zn et Mn, basées sur l'hydrolyse sont inexactes.—G. VAN PELT.

Many salt solutions are decomposed by the action of water. The phenomenon is termed **hydrolysis.** Thus, bismuth and antimony chlorides with water form insoluble oxychlorides; mercuric sulphate forms a basic sulphate; and boiling solutions of ferric chloride form a mixture of ferric hydroxide and a basic ferric chloride, together with free hydrochloric acid.[1] It is possible to draw up a list of salts where the phenomenon is marked and well-defined at one end of the series, and at the other end the hydrolysis is but ill-defined and feeble. In the former case the reaction is quantitative, and may be used in analytical separations; in the latter case the separations are incomplete.

It will be seen that an acid is usually one product of the hydrolysis. For instance, the hydrolysis of titanic sulphate is represented in symbols—

$$Ti(SO_4)_2 + 4H_2O \rightleftharpoons 2H_2SO_4 + Ti(OH)_4$$

Titanium hydroxide—$Ti(OH)_4$—is soluble in the free acid, but at first the rate at which the sulphate is decomposed is much greater than the rate of dissolution of the hydroxide by the acid. Hence, acid accumulates in the solution. As the acid accumulates in the solution, its effects become more and more marked, and finally, when the free acid has attained a certain concentration, the speeds of the two reactions will be equal, and no further separation of the hydroxide will be observed, because it will be dissolved by the free acid as fast as it is formed.

Similar remarks apply to salts of the tervalent metals, iron, aluminium and chromium.[2] Their equilibrium conditions are symbolised:

$$XCl_3 + 3HOH \rightleftharpoons X(OH)_3 + 3HCl$$

To drive the reaction completely from left to right it is necessary to remove the free acid as fast as it is formed. Several methods have been proposed.

1. *By Weak Bases.*—When weak bases—aniline, ammonia, phenylhydrazine, hexamethylenetetramine—are present, some of the liberated acid is converted into a neutral salt of the base.[3] The concentration of the free acid is thus diminished, and a much greater proportion of the hydroxide will separate. If a sufficient quantity of the base be present to prevent the acid accumulating in the system, all the salt may be hydrolysed. The salt—say ammonium chloride, NH_4Cl—formed by the union of the base with the free acid may itself be hydrolysed by the water:

$$H_2O + NH_4Cl \rightleftharpoons NH_4OH + HCl$$

Hence, there is a limit to the extent to which the base can neutralise the free acid. In the case of the alumina precipitation, there is nearly always enough free acid present to prevent the hydrolysis of the magnesium salts, whereas with aluminium, titanium, zirconium, chromium, beryllium, thorium, cerium

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[1] For the hydrolysis of iron salts, see U. Antony and G. Gigli, *Gazz. Chim. Ital.*, **26**, 1, 293, 1896; U. Antony, *Rend. Accad. Lincei*, (5), **5**, 197, 1896; H. M. Goodwin, *Zeit. phys. Chem.*, **21**, 1, 1896.

[2] G. van Pelt, *Bull. Soc. chim. Belg.*, **28**, 101, 1914.

[3] For the precipitation of zinc salts with dimethylamine, see W. Herz, *Zeit. anorg. Chem.*, **26**, 90, 1901; and for magnesium salts with dimethylamine and piperidine, see W. Herz and K. Drucker, *ib.*, **26**, 347, 1901; W. Herz, *ib.*, **27**, 310, 1901; **30**, 280, 1902; A. Hantzsch, *ib.*, **30**, 289, 1902.

and ferric salts the liberated hydroxide can exist in the presence of the small amount of free acid produced by the hydrolysis of the ammonium salt. The complete separation of these hydroxides thus depends upon the extent to which the salt, formed by the combination of the freed acid with the base, is hydrolysed. With aniline more free acid will be formed in the system than with phenylhydrazine, and with phenylhydrazine more than with ammonia. Hence, hydroxides completely precipitated by ammonia may be only partially precipitated by phenylhydrazine, and not at all by aniline. With beryllium chloride, for example, the hydroxide is completely precipitated by phenylhydrazine, but not by aniline, and ferric iron is precipitated by ammonia, but not by phenylhydrazine. The nature of the acid is of great importance, since the salts of one acid may be more susceptible to hydrolysis than the salts of another. Thus, complete precipitation may occur with beryllium chloride, while but a trace is precipitated with the nitrate.[1]

2. *By an Insoluble Carbonate—Barium or Calcium.*—The mechanism of the reaction is fairly simple here, the free acid, say hydrochloric acid, reacting as symbolised—

$$BaCO_3 + 2HCl = BaCl_2 + CO_2 + H_2O$$

and the chlorides of barium and calcium are very feebly hydrolysed in solution. The method is discussed on page 522.

3. *By a Mixture of Potassium Iodate and Iodide.*—This method, due to Stock,[2] is based on the reaction:

$$KIO_3 + 5KI + 6HCl = 6KCl + 3I_2 + 3H_2O$$

Hence, aluminium hydroxide is quantitatively precipitated by the mixture in question:

$$Al_2(SO_4)_3 + 5KI + KIO_3 + 3H_2O = 2Al(OH)_3 + 3K_2SO_4 + 3I_2$$

It was found advantageous to use either sodium thiosulphate or an excess of potassium iodide so as to prevent the separation of solid iodine. Stannous salts and those of chromium, cobalt, nickel, zinc and some of the rare earths also react quantitatively. The process does not work well with iron salts as ferric salts are reduced to the ferrous state by potassium iodide and ferrous salts are but little hydrolysed.

4. *By Sodium Acetate in the presence of Acetic Acid.*—The reaction is here a little curious, for at first sight the mixture does not seem as if it would neutralise free acids. The sodium unites with the mineral acid liberated by the hydrolysis and the liberated acetic acid ultimately forms, say, ferric acetate, a salt which is virtually hydrolysed completely on warming the solution—*vide* p. 382. Acids other than acetic—*e.g.* formic, succinic and benzoic acids—can be used, but acetic acid is the favourite, and bases other than sodium—*e.g.* ammonium—have been tried.

The general principles here indicated may, of course, be modified in special cases, because of the formation of double or basic salts. For instance, some authors attribute the effect of ammonium salts, in retarding the precipitation of magnesium hydroxide by ammonia, to the formation of the complex salt——$Mg(NH_4)_2Cl_4$—which is not decomposed by ammonia. As a matter of fact,

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[1] A. M. Jefferson, *Journ. Amer. Chem. Soc.*, **24**, 540, 1902; B. L. Hartwell, *ib.*, **25**, 1128, 1903; E. T. Allen, *ib.*, **25**, 421, 1903; W. H. Hess and E. D. Campbell, *ib.*, **21**, 776, 1889.
[2] A. Stock, *Compt. rend.*, **130**, 175, 1900; S. E. Moody, *Amer. Journ. Science*, (4), **20**, 181, 1905; (4), **22**, 176, 1906; S. H. Katz and C. James, *Journ. Amer. Chem. Soc.*, **36**, 779, 1914.

ammonia, in the absence of ammonium salts, precipitates half the magnesium as hydroxide, and the other half as the complex salt. It is then supposed that the addition of an ammonium salt dissolves the hydroxide with the formation of more $Mg(NH_4)_2Cl_4$. The accumulation of ammonium chloride [1] in the system will also lessen the amount of the hydrolysed salt.[2] Similar remarks might be applied to manganese salts. With zinc,[3] cobalt [4] and nickel [5] complex salts may be formed, so that both influences indicated above come into play.

§ 81. The Determination of the Ammonia Precipitate.

First Precipitation.—Two to three grams of solid ammonium chloride [6] are added to the filtrate from the silica, in a 400 c.c. beaker, and the solution is heated to 80°–90°.[7] Aqueous ammonia is then added in slight excess.[8] The ammonia is added slowly and with constant stirring in order to prevent bubbles of gas violently projecting some of the hot liquid from the beaker. Let the precipitate settle for five minutes, but no longer, and then filter promptly through, say, a 12·5 cm. filter-paper,[9] and wash four times by decantation [10] with a hot solution of ammonium nitrate [11] in order to coagulate the gelatinous precipitate. The filter-paper is washed at the same time.

[1] J. M. Lovén, *Zeit. anorg. Chem.*, **11**, 404, 1896; F. P. Treadwell, *ib.*, **37**, 326, 1904; W. Herz and G. Muhs. *ib.*, **38**, 138, 1904; W. Herz, *ib.*, **21**, 243, 1899; **22**, 279, 1900; **23**, 222, 1900; **24**, 123, 1900; D. E. Dionisiey, *Journ. Russ. Phys. Chem. Soc.*, **45**, 905, 1913.

[2] Usually the solution contains sufficient hydrochloric acid to form enough ammonium chloride with the ammonia to prevent the precipitation of the magnesium hydroxide. A. A. Noyes, W. C. Bray, and E. B. Spears (*Tech. Quart.*, **21**, 14, 1908; *Journ. Amer. Chem. Soc.*, **30**, 481, 1908) state that 0·005 grm. of magnesium chloride made up with 5 c.c. of hydrochloric acid (sp. gr. 1·12) to 100 c.c. gave no precipitate with 40 c.c. of ammonia (sp. gr. 0·96), but a precipitate appeared with 50 c.c. of ammonia.

[3] W. Herz, *Zeit. anorg. Chem.*, **25**, 225, 1900; W. Gaus, *ib.*, **25**, 236, 1900; W. Bonsdorff, *ib.*, **41**, 132, 1904; H. Euler, *Ber.*, **36**, 3400, 1903.

[4] A. Werner, *Ber.*, **40**, 15, 1907.

[5] H. M. Dawson and J. M'Crae, *Journ. Chem. Soc.*, **77**, 1239, 1900; W. Bonsdorff, *Zeit. anorg. Chem.*, **41**, 132, 1904; M. Konowaloff, *Chem. Centr.*, (1), 646, 1900.

[6] The object of the ammonium chloride is to retard the precipitation of magnesium and manganese hydroxides, as indicated above.

[7] W. E. Taylor (*Chem. News*, **103**, 169, 1911) claims that adding the ammonia to the solution at 66°, and then raising the temperature to the boiling-point, gives a more granular precipitate than adding ammonia to the boiling solution.

[8] W. Blum (*Journ. Amer. Chem. Soc.*, **38**, 1282, 1916) states that complete precipitation occurs at p_H 6·5 to 7·5. Hence, to the solution he adds 5 grams of ammonium chloride and a few drops of a 0·2 per cent. alcoholic solution of phenol red. Ammonia is then added to the boiling solution until the colour turns red. The use of the term "excess" in analytical chemistry often misleads beginners. It is comparatively rare to find reactions in which complete precipitation is effected by adding the theoretical amount of the precipitating agent. When such reactions are known, they generally make useful volumetric processes. In most cases, more of the precipitating agent must be added than satisfies the regular type of equation representing the reaction. *The term "excess" means that enough precipitating agent must be added to ensure complete precipitation—and no more.* As J. W. Mallet used to say, *ad maxima per minima.* Analytical chemistry has not yet reached that stage where it can answer, for each reaction, the following types of question: What amount constitutes an excess? How does this excess differ when different salts are present? Does the presence of certain salts diminish the amount of the "excess" needed?

[9] For china clays use a 12·5 cm. paper; for Cornish stone, an 11 cm. paper; and for glazes and siliceous clays, a 9 cm. or even a 7 cm. paper will be ample; see page 79.

[10] With many clays the precipitate settles too slowly for washing by decantation.

[11] AMMONIUM NITRATE SOLUTION.—Neutralise 20 c.c. of concentrated nitric acid with ammonia, and dilute to a litre (R. Bunsen, *Liebig's Ann.*, **106**, 13, 1858; S. L. Penfield and D. N. Harper, *Amer. J. Science*, (3), **32**, 112, 1886; *Chem. News*, **54**, 90, 102, 1886; L. Muravlev and O. Krassnovski, *Zeit. anal. Chem.*, **69**, 389, 1916). A few drops of litmus will indicate whether the solution be acid. An acid solution is, of course, fatal to success.

Second Precipitation.—A hole is made through the apex of the filter-paper and as much as possible of the precipitate is washed through into the beaker from which it has just been filtered. Hot dilute (1 : 1) hydrochloric acid is then run through the filter-paper into the beaker; finally the paper is washed free from chlorides and retained for subsequent ignition. The precipitate dissolves in the acid solution and washings from the filter-paper.[1] The precipitation with ammonium chloride and ammonia is repeated. The precipitate is washed as before four times by decantation, with the ammonium nitrate solution, the washings being passed through another filter-paper. The precipitate is then transferred to this filter-paper,[2] and washed with the hot solution of ammonium nitrate until the washings are free from chlorides when a few drops of them, acidified with nitric acid, are tested with silver nitrate.[3] It is highly important to note that the ammonia precipitate must never be allowed to run dry during washing, otherwise it is practically impossible to remove the last traces of chlorides.

Recovery of Alumina and Silica from the Filtrate.—Towards the end of the washing, a re-solution of part of the alumina precipitate sometimes takes place.[4] In any case some alumina and silica[5] are generally found in the filtrate. These must be recovered. Evaporate the filtrate to about 50 c.c.,[6] add 2 to 3 c.c. of ammonia and boil off all but the last traces of ammonia. The precipitate is now filtered through a 7 cm. filter-paper and washed free from chlorides with hot ammonium nitrate solution. The filtrate and washings, which are used for the determination of lime and magnesia, are collected in a 250 c.c. beaker.[7]

Ignition of the Precipitate.—After the precipitates have drained, the three filter-papers and their contents are transferred, while still moist, to the platinum crucible containing the residue from the silica.[8] The precipitate and papers are gently heated above a Bunsen burner, fitted with a mushroom head, until

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[1] Freshly precipitated aluminium and ferric hydroxides are readily soluble in dilute acids, but after standing a short time they take a long time to dissolve—M. Jeannel, *Compt. rend.*, 66, 799, 1868; J. Attfield, *Chem. News*, 17, 303, 1868. Hence the need for speedy work. To facilitate the solution of gelatinous precipitates, F. A. Gooch (*Amer. J. Science* (4), 20, 11, 1905; *Chem. News*, 92, 64, 1905) uses a cone of platinum gauze between the filter-paper and the precipitate. Most of the precipitate can then be lifted with the cone from the paper and transferred to the beaker for solution—P. T. Austen, *Chem. News*, 38, 88, 1878.

[2] Instead of the "policeman," a swab made from a quarter of a 7 cm. paper may be rubbed against the sides of the beaker and transferred to the filter-paper. The swabbing is repeated with each of the other three quarters.

[3] For the difficulty in washing out the last traces of chloride, see L. T. Wright, *Journ. Chem. Soc.*, 43, 156, 1883.

[4] When water alone is used for washing, or if the ammonium nitrate solution becomes acid. For the solubility of aluminium hydroxide in water and ammonia solutions, see G. Jander and O. Ruperti, *Zeit. anorg. Chem.*, 153, 253, 1926, and page 158.

[5] For the solubility of silica in aqueous ammonia, and water, see W. Skey, *Chem. News*, 17, 165, 1868; A. M. Edwards, *ib.*, 73, 13, 1896; R. Pribram, *Wittstein's Viertel.*, 16, 30, 1867; *Chem. News*, 17, 227, 1868; A. Souchay, *Zeit. anal. Chem.*, 11, 187, 1872; G. Karsten, *Pogg. Ann.*, 6, 357, 1826.

[6] It is best to evaporate the main filtrate and washings separately. The washings are taken to dryness, and the ammonium salts driven off.

[7] F. Muck (*Zeit. anal. Chem.*, 19, 140, 1880) recommends removing the sodium and potassium chlorides which accumulate in the solution—particularly after the "basic acetate separation" (page 381)—by evaporating the solution to dryness, dissolving the residue in concentrated hydrochloric acid, and washing the residual salts with concentrated acid on a glass-wool filter. There is, however, rarely any occasion for this operation. Ammonium salts are usually removed by evaporation to dryness and direct volatilisation, or by heating with nitric acid (H. Jervis, *Chem. News*, 86, 271, 1902), or with some nitrous acid (P. Jannasch, *Journ. prakt. Chem.*, (2), 72, 38, 1905).

[8] For the effect of ammonium chloride, see H. W. Daudt, *Journ. Ind. Eng. Chem.*, 7, 847, 1915.

quite dry,[1] and then the heat is increased to char the papers.   The mushroom head is removed, the crucible [2] placed in a slantwise position on the triangle, to permit free access of air, and heated to red heat until all the carbon is burnt off.   This is followed by 15 minutes' blasting, or heating over a Méker burner, with the lid of the crucible on.   The alumina is not properly dehydrated if heated on the ordinary Bunsen burner.[3]   Let the crucible cool in a desiccator. Moisten the cold mass with a drop of concentrated nitric acid, and heat gently until no more fumes are evolved.   Re-ignite, cool and weigh.[4]   The weight of the crucible and contents, less the weights of the empty crucible, the "extra" silica (see page 167) and the ashes from the filter-papers, used in the silica and alumina determinations,[5] gives the weight of the alumina, ferric oxide,[6] titanic oxide and phosphoric oxide (if present) in the precipitate.[7]   When much ferric oxide is present, the results will be low, owing to the reduction of ferric oxide if a covered crucible, placed vertically, is surrounded by the flame.   Hence it is important to place the crucible so that there is a free circulation of air inside.[8]

Dissolution of the Ignited Precipitate.—The precipitate dissolves so slowly in acids that it is necessary to fuse the ignited precipitate with about six times

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[1] With highly ferruginous clays it is best to dry the precipitate in an air bath at about 110°, and ignite the paper separately in order to prevent the reduction of the ferric oxide by the carbon of the paper.   The magnetic oxide of iron formed by the reduction cannot easily be re-oxidised to Fe_2O_3, since it is protected from the air when buried in the alumina.   Alumina, however, "decolorises" the ferric oxide and retards the reduction to magnetic oxide (H. Warth, *Chem. News*, 84, 305, 1901); indeed, a mixture of alumina with 6·8 per cent. of Fe_3O_4 after ignition contained only ferric oxide.   If the alumina has been precipitated with paper pulp, this precaution is not required, since the precipitate is then fine enough and open enough to re-oxidise readily, even if it be partly reduced.   W. Suida (*Tschermak's Mitt.*, (1), 5, 176, 1876) has shown that ferric oxide is stable on calcination in a Bunsen burner if reducing agents be excluded (H. Rose, *Pharm. Centr.*, (1), 19, 488, 1848).   C. Bodewig (*Zeit. Kryst.*, 7, 176, 1883) states that there is always a certain amount of reduction in platinum crucibles, even when the crucible is but half covered with a sloping lid, since the ignited precipitate, when taken up with hydrochloric acid, gives a blue coloration with potassium ferricyanide.   H. St C. Deville and L. Troost (*Compt. rend.*, 56, 977, 1863) have shown that platinum is permeable to the flame gases at high temperatures (see page 395).   Bodewig prefers to ignite the precipitate in a porcelain crucible, moisten with nitric acid, dry, ignite and weigh.   This sequence of operations is repeated a second time.   The oxide thus obtained is said to be free from ferrous oxide.   L. Vásárhely (*Zeit. anal. Chem.*, 53, 688, 1914) recommends ignition in a Rose's crucible in a current of oxygen to prevent the formation of magnetite.

[2] H. von Jüptner (*Chem. Ztg.*, 13, 1303, 1889) has devised a little asbestos cover for crucibles which accelerates the combustion of filter-papers and of organic matter during ignitions.

[3] A. Mitscherlich, *Zeit. anal. Chem.*, 1, 67, 1862; E. T. Allen and V. H. Gottschalk, *Amer. Chem. Journ.*, 24, 292, 1900; E. T. Allen and H. F. Rogers, *ib.*, 24, 304, 1900; W. Biltz, *Zeit. angew. Chem.*, 43, 370, 1930; K. Zimmermann, *Chem. Weekb.*, 31, 317, 1934; but see page 153.

[4] For the hygroscopicity of ignited alumina, see G. A. Kall, *Sprechsaal*, 59, 313, 1926; H. S. Taylor and A. J. Gould, *Journ. Amer. Chem. Soc.*, 56, 1685, 1934.

[5] Note that the two filter-papers from the silica filtration have been in contact with acid liquids, and the three papers from the alumina filtration with alkaline liquids—see p. 79, Table XIII.   The ash from high-grade filter-papers is not necessarily free from silica.   The amount is usually so small that no appreciable error is introduced by deducting the total weight of the five filter ashes from the weight of the ammonia precipitate, though the silica from the papers used in the silica filtration will have been eliminated during the evaporation to dryness with hydrofluoric acid.

[6] Ferric oxide sometimes stains the platinum crucible badly (see page 98).   This stain can generally be removed by letting the crucible stand overnight in contact with concentrated hydrochloric acid, and then warming it for a short time.   Fused potassium bisulphate or pyrosulphate will also clean off the iron stain.

[7] Here, too, will be found, if present: columbium, tantalum, tungsten, zirconium, hafnium, beryllium, chromium, thorium and the rare earths.   In the rare event of a determination of these constituents being required, see the later pages of this work.

[8] E. Selch (*Zeit. anal. Chem.*, 54, 457, 1915).

its weight of potassium pyrosulphate.[1] The preliminary heating, especially if potassium bisulphate be used in place of the pyrosulphate, must be very gradual in order to avoid loss by the spattering of the fused mass.[2] The covered crucible is heated over a small flame until the contents are melted. The crucible is then raised six or nine inches above the flame, when the moisture can then be driven off without danger. The crucible can be lowered nearer the flame in a short time.[3] If any particles of the precipitate adhere to the sides, wash them down by imparting a rotary motion to the contents of the crucible, or tilt the crucible a little to permit the fused salt to act on the grains. Slowly raise the temperature until the bottom of the crucible shows faint redness, but watch carefully to prevent frothing. If the crucible be lifted away with the tongs, and the contents of the cooling crucible be watched in a good light, it will be easy to see through the transparent mass if all is dissolved. Heat the crucible a few minutes more, even if all has dissolved.[4] Cool by placing the crucible on a cold slab. When cold, half-fill the crucible with cold water and heat it over the tip of a small flame. The cake soon comes away from the crucible. It is then dissolved in water containing about 10 c.c. of concentrated sulphuric acid.[5] The cake dissolves quicker on warming, but if the solution be boiled, titanium oxide may be precipitated. It is well to know how much acid and pyrosulphate have been used, so that an allowance can be made later on when dealing with the titanium.

Correction for Silica.—The solution formed by the dissolution of the cake is evaporated on a water bath to a small volume and then heated on a sand bath until fumes of sulphuric acid come off copiously.[6] Sufficient sulphuric acid should be present to form a paste when the mass is cold. The residue is digested at a low temperature (40° to 50°) with water on a water bath until all the sulphates have passed into solution, and the silica which separates is then filtered off, washed, ignited and weighed.[7] The weighed residue is treated with hydrofluoric acid, as indicated on page 149, ignited and re-weighed. The difference in the two weighings is called the "extra silica"; its

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[1] Where a pyrosulphate fusion has not been preceded by a hydrofluoric acid evaporation, a silica crucible can be advantageously used instead of a platinum one.—W. R. Schoeller, *Analyst*, 56, 305, 1931; A. K. Lyle, *Journ. Amer. Cer. Soc.*, 15, 334, 1932.

[2] The pyrosulphate gives less trouble in this respect, but only the purest grade obtainable must be used. In particular the salt must be free from iron compounds and silica, both of which are fatal to accurate work. To convert potassium bisulphate to the pyrosulphate, melt the bisulphate in a platinum dish, and when the spluttering has ceased and white fumes begin to come off freely, pour the fused mass into another dish. When cold, the pyrosulphate can be easily broken into pieces and bottled. J. L. Smith (*Amer. J. Science*, (2), 40, 248, 1865) preferred the sodium salt. It acts more rapidly than the potassium salt, and also forms a more suitable cake. It is, however, liable to crust over during the fusion; and the cold cake is not so easily detached from the crucible as when potassium pyrosulphate is used. It can be adopted with advantage. E. Deussen (*Zeit. anorg. Chem.*, 44, 423, 1905) recommended acid potassium fluoride with the idea of eliminating the solvent action of the pyrosulphate on the platinum. This salt is not to be recommended in accurate silicate analyses, because (1) the "extra silica" is lost; and (2) the fluorine, unless expelled, later on interferes with the permanganate titration and the titanium determination.

[3] Half an hour, if potassium bisulphate be used instead of the pyrosulphate.

[4] If the mass be heated too strongly and normal potassium sulphate be formed, the small contraction of the cooling sulphate and the relatively large contraction of the crucible may cause the crucible to burst.

[5] E. Hart (*Journ. Anal. App. Chem.*, 2, 410, 1888) adds concentrated sulphuric acid in excess and warms the mixture until the mass is dissolved. When cold, dilute with water and neutralise the excess of acid with sodium carbonate.

[6] W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, 700, 117, 1919. If the mass darkens, platinum, derived from the crucible during the bisulphate fusion, is separating.

[7] See also J. A. Phillips, *Phil. Mag.*, (4), 41, 87, 1871.

weight is to be subtracted from the weight of the precipitate, as indicated on page 166, and added to the corrected silica of page 151. The residue in the crucible is fused with a little more pyrosulphate, and the cold mass, after dissolving in dilute sulphuric acid, added to the main solution,[1] which is made up to 250 c.c. in a graduated flask.

Correction for Barium.—If traces of barium be retained by the silica and the alumina precipitates they will be found in the residue in the crucible left after determining the "extra silica." Hence, if barium be present it will remain as insoluble sulphate when the cake from the pyrosulphate fusion is dissolved up. In such cases the barium sulphate is collected on a 7 cm. filter-paper, washed, ignited and weighed (page 703).[2] The filtrate is then added to the main solution.

Correction for Platinum from the Crucible.—In exact analyses provision for the removal of platinum should always be made after a pyrosulphate or a bisulphate fusion. Platinum is readily precipitated from hot sulphate solutions by hydrogen sulphide and subsequent ignition of the washed precipitate leaves metallic platinum. Some platinum may be found in the filtrate from the silica, but it is not usually necessary to remove it at this stage of the work. Hence all the platinum is not necessarily derived from the crucible during the pyrosulphate fusion, and, in consequence, if the platinum be weighed in the same crucible as that in which the bisulphate fusion was made, any excess over that lost by the crucible should be deducted from the alumina.[3]

Errors.—Eight independent determinations, using the same clay as that mentioned on page 151, gave the following numbers for the "ammonia" precipitate:—

0·2460; 0·2452; 0·2474; 0·2458; 0·2447; 0·2461; 0·2465; 0·2457,

with a mean value of 24·59 per cent., and a deviation of approximately ±0·13.

The chief sources of error are: (1) Imperfect precipitation of the alumina and iron;[4] (2) Imperfect washing of the precipitate; (3) Precipitation of lime owing to the use of ammonia contaminated with ammonium carbonate (*v.* page 158); (4) Imperfect dehydration; (5) Variable state of oxidation of the iron on ignition; (6) Contamination with silica subsequently dissolved in the bisulphate fusion. The imperfect washing is probably the most serious error. The alumina determination is the *pons asinorum* of clay and silicate analysis.[5]

The iron (page 169), manganese (page 394), phosphoric oxide (page 672), and titanium (page 189) are now determined in aliquot portions of the acid solution of the pyrosulphate fusion. The corrections for vanadium, rare earths, beryllium, uranium and chromium are discussed in the chapters dealing with these elements.

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[1] According to W. F. Hillebrand (*Journ. Amer. Chem. Soc.*, **24**, 369, 1902; *Chem. News*, **86**, 90, 1902), from one to two milligrams of silica still remain in solution and escape recovery.

[2] If an appreciable amount be present, it is well to prove that it really is barium sulphate by fusion with sodium carbonate, etc. If phosphoric acid be present, some titanium phosphate may be precipitated, and this may be mistaken for barium sulphate.

[3] L. Brandt, *Chem. Ztg.*, **39**, 553, 1915.

[4] G. Jander and E. Wendehorst, *Zeit. angew. Chem.*, **35**, 244, 1922; G. Jander and B. Weber, *Zeit. anorg. allgem. Chem.*, **131**, 266, 1923.

[5] For a critical study of the determination of aluminium, see L. A. Congdon and J. A. Carter, *Chem. News*, **128**, 98, 1924; also J. E. Clennell, *Journ. Inst. Metals*, **28**, 253, 1922; *Journ. Soc. Chem. Ind.*, **41**, 418 R, 1922; *Mining Mag.*, **22**, 88, 1920.

CHAPTER XIV.

THE DETERMINATION OF IRON.

§ 82. The Determination of Iron.

THERE is a wide choice of methods for the determination of iron depending upon volumetric, colorimetric or gravimetric processes. In volumetric processes the ferric iron may be reduced to the ferrous condition by reagents such as stannous chloride, metallic zinc, copper,[1] hydrogen sulphide or chromous sulphate.[2] The special features of the different processes of reduction here recommended are indicated later. The ferrous salt is re-oxidised to the ferric condition by a standard solution of potassium permanganate, potassium dichromate or ceric sulphate. The iron can also be determined volumetrically while in the ferric condition by titration with titanous chloride, which reduces the ferric to the ferrous condition during the titration.[3] Störmer [4] has compared permanganate and dichromate titrations with Rothe's ether process and pronounces in favour of the permanganate titration. The permanganate process has long been a favourite on account of its simplicity, accuracy and elegance, and it is the best process to use when the conditions are favourable; but unfortunately, as we shall soon see, it is not always satisfactory in clay analyses. The colorimetric process (page 185) has the advantage that the iron is directly determined in the ferric condition, without reduction, and it is quite satisfactory, both in speed and accuracy, for general work on clays containing less than about 5 per cent. of ferric oxide. For gravimetric processes, see pages 503 *et seq.*

§ 83. The Reduction of the Ferric to Ferrous Salts for the Permanganate Titration.

Reduction by Metallic Zinc or Magnesium.—Zinc, in spite of many objections, is the favourite method of reduction. The filtrate from the bisulphate fusion is treated with iron-free zinc [5] and dilute sulphuric acid until a drop removed on

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[1] G. Scagliarini and P. Pratesi, *Ann. Chim. applicata*, **19**, 85, 1929.
[2] W. M. Thornton, jun., and J. F. Sadusk, jun., *Ind. Eng. Chem. Anal. Ed.*, **4**, 240, 1932.
[3] A. Purgotti titrates ferric solutions with an acid solution of molybdenum oxide—Mo_3O_8 (*Gazz. Chim. Ital.*, **26**, ii., 197, 1896).
[4] M. Störmer, *Tonind. Ztg.*, **32**, 1609, 1908; R. Davidson, *Journ. Soc. Chem. Ind.*, **6**, 421, 1887; P. Lehnkering, *Zeit. öffent. Chem.*, **4**, 459, 1898.
[5] It is not easy to get zinc free from iron and carbon. G. F. Rodwell (*Chem. News*, **3**, 4, 1861) found that zinc contained about 1·3 per cent. of a black insoluble residue consisting of about 0·5 per cent. of carbon along with some lead and iron. Carbon, if present, decolorises a certain amount of permanganate, and gives high results (J. B. Mackintosh, *Chem. News*, **50**, 75, 1884). It is generally advisable to make a blank test with, say, 10 grms. of the zinc, and thus find a correction for the zinc used in the reduction. If the zinc be pure, it dissolves very slowly in acids, and even when the pure zinc is in contact with platinum a reduction may

a glass rod gives no reddish-brown coloration with a drop of ammonium thiocyanate. This method is convenient and extensively used when the titanium is ignored.

The solution under investigation is placed in an Erlenmeyer flask. The solution should not contain more than about $0 \cdot 1$ grm. of Fe_2O_3 per 100 c.c.[1] Add some thin flakes of granulated zinc, or, better still, two or three portions of
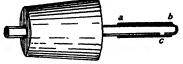
FIG. 66.—Bunsen's Valve.   FIG. 67.—Binder's Valve.

stick magnesium.[2] Add sufficient sulphuric acid to make a solution containing about 17 per cent. of H_2SO_4.[3] The flask is closed with a one-hole rubber stopper fitted with a Bunsen's (fig. 66) or a Binder's valve (fig. 67),[4] or, better,

occupy 24 hours. L. Moyaux (*Rev. Univ. Mines*, (1) **25**, 148, 1869) recommends amalgamated zinc. Amalgamated zinc in contact with platinum is better, but the action may stop owing to the amalgamation of the platinum during the action (A. L. Beebe, *Chem. News*, **53**, 269, 452, 1886). To amalgamate zinc, shake it in a flask with a solution of mercuric sulphate in $2 \cdot 5$ per cent. sulphuric acid (1 grm. metallic mercury per 100 grms. of zinc). Wash the metal several times with $2 \cdot 5$ per cent. sulphuric acid, and finally with water. See also footnote 1, p. 184. G. T. Morgan (*Analyst*, **26**, 225, 1901; J. H. Gladstone, *Chem. News*, **32**, 75, 195, 1875; J. H. Gladstone and A. Tribe, *ib.*, **32**, 150, 1875) recommends a zinc-copper couple in a 3 per cent. solution of sulphuric acid. The zinc-copper couple is made by immersing, say, 8 grms. of granulated zinc in 200 c.c. of a 10 per cent. solution of copper sulphate. The action is said to be much more rapid than with zinc alone. For the aluminium reduction in hot solutions, see F. J. R. Carulla, *Journ. Soc. Chem. Ind.*, **27**, 1049, 1908; W. H. Seamon, *Chem. Eng.*, **8**, 124, 1908; C. L. Schumann, *Journ. Ind. Eng. Chem.*, **7**, 431, 1915. Aluminium foil does its work more rapidly than zinc, but it too must be corrected for iron. Magnesium ribbon is generally free from iron, phosphorus and sulphur. It reduces much more rapidly than zinc (S. Kern, *Chem. News*, **33**, 112, 1876; H. N. Warren, *ib.*, **60**, 187, 1889), but is liable to float on the surface of the solution. This objection does not apply to sticks of metallic magnesium, which is in many ways preferable to zinc—but the cost is a little greater. A. Gemmell (*Analyst*, **35**, 65, 1910) recommends zinc-aluminium and magnesium-aluminium (magnalium) alloys for some reductions. For reductions with palladium-hydrogen, see L. Kritschewsky, *Ueber die Anwendung des metallischen Wasserstoffs in der analytischen Chemie*, Bern, 1885; W. H. Gintl, *Zeit. angew. Chem.*, **15**, 424, 1902; A. C. Chapman, *Analyst*, **29**, 346, 1904. For the efficiency of different reducing agents, see A. C. Chapman and H. D. Law, *ib.*, **31**, 3, 1906. For reduction with metallic copper, see L. Storch, *Ber. Oester. Ges. Förder. Chem. Ind.*, **15**, 9, 1893; W. C. Birch, *Chem. News*, **99**, 273, 1909. J. C. Hostetter (*Journ. Washington Acad. Sci.*, **3**, 429, 1913; *Chem. News*, **108**, 239, 1913) and H. C. Allen (*Journ. Amer. Chem. Soc.*, **36**, 937, 1914) recommend reduction by electrolysis. For reduction by cadmium amalgam, see J. H. Capps and O. W. Boies, *Journ. Phy. Chem.*, **19**, 65, 1915.

[1] A. Mitscherlich (*Zeit. anal. Chem.*, **2**, 72, 1863) says that there is a danger of loss owing to the precipitation of some metallic iron on the zinc—N. W. Fischer, *Pogg. Ann.*, **9**, 266, 1827. The iron dissolves when the last trace of zinc dissolves. There is, however, no danger under this head when the solutions are diluted and acidified as indicated in the text. E. Müller and G. Wegelin (*Zeit. anal. Chem.*, **50**, 615, 1911) note the danger indicated by Mitscherlich, and recommend reducing the ferric iron by adding 5–10 drops of N-$CuSO_4$ and warming the solution with amalgamated zinc rods for a couple of hours.

[2] 10 grms. of metallic zinc, or 4 grms. of metallic magnesium, usually suffice for reducing $0 \cdot 1$ grm. of ferric oxide.

[3] That is, about 20 c.c. of concentrated sulphuric acid per 100 c.c. of the solution (sp. gr. $1 \cdot 8$). Note the amount of acid already present in the solution. A. Leclèrc (*Journ. Pharm. Chim.*, (7), **7**, 587, 1913) adds ammonium sulphate, since the ferrous ammonium sulphate formed oxidises much less quickly than ferrous sulphate solutions.

[4] For a Bunsen's valve (fig. 66), fit the hole in the stopper with a short piece of glass tubing (*a*, fig. 66), to which is attached a piece of indiarubber tubing plugged at the other end with a piece of glass rod (*b*). The rubber tubing has a longitudinal slit (*cd*). It readily permits the outflow of gas, but offers some opposition to the back flow of air. The valve will sometimes hold so well that the flask will break before the valve gives way, particularly when the contents

with a Kempf's or a Schiebler's gas-washer as guard tube.[1] These vessels are glass bulbs fitted inside with a syphon tube as shown in fig. 68. When the iron is reduced, an aqueous solution of sodium bicarbonate is poured into the bulb until the free end of the inner tube just dips below the surface. As the flask cools, the bicarbonate solution is drawn into the flask, and carbon dioxide is given off. When equilibrium is established, the contents of the flask are well protected from the air by the carbon dioxide. The flask may be warmed to facilitate the reduction. The reduction is complete when a drop of the solution gives no red coloration with a drop of ammonium thiocyanate.[2] The flask may be heated until all the zinc is dissolved; [3] or the undissolved zinc and carbon may be filtered off through glass-wool. There is, however, a great risk of re-oxidation during the filtration. If the titanium is to be neglected, the solution can be titrated at once with standard permanganate as described below.

FIG. 68.—
Schiebler's
Guard Tube.

Effect of Titanium.—When titanium is present,[4] the zinc reduces, more or less completely,[5] the titanic oxide to titanium sesquioxide : $2TiO_2 \rightarrow Ti_2O_3$. The latter is re-oxidised to titanic oxide, TiO_2, during the permanganate titration.[6] In consequence, more or less [7] titanium is estimated as if it were iron. It is by no means uncommon to find clays with $\frac{1}{2}$ to 4 per cent. of titanic oxide, and such clays would be reported with $\frac{1}{2}$ to 4 per cent. of ferric oxide

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of the flask have been heated and allowed to cool with the Bunsen's valve in position. R. Fresenius, *Anleitung zur quantitativen chemischen Analyse*, Braunschweig, 278, 1853; A. Krönig, *Pogg. Ann.*, 122, 170, 1864; C. H. Bostock, *Chem. News*, 57, 213, 1890; U. Kreusler, *Zeit. anal. Chem.*, 24, 393, 1885; O. Binder, *ib.*, 27, 178, 1888; O. Reitmar and A. Stützer, *Rep. anal. Chem.*, 5, 232, 1885; L. R. Milford, *Journ. Ind. Eng. Chem.*, 4, 845, 1912. The construction of Binder's valve will be obvious from fig. 67, where *c* represents a small aperture in the side of a glass tube closed at one end; and *ab*, a piece of rubber tubing.

[1] T. Kempf, *Zeit. anal. Chem.*, 7, 442, 1868; W. T. K. Stock, *Chem. News*, 39, 46, 1879; R. Jahoda, *Zeit. angew. Chem.*, 2, 87, 1889; H. Göckel, *ib.*, 12, 620, 1899; *Chem. Ztg.*, 37, 235, 1913; A. Contat, *ib.*, 22, 298, 1898; M. Spang, *ib.*, 36, 1465, 1912; M. Mittenzwey, *Journ. prakt. Chem.*, (1), 91, 86, 1864. Several other devices have been used.

[2] This test will indicate one part of iron in 1,600,000 parts of water—A. Wagner, *Zeit. anal. Chem.*, 20, 349, 1881; E. F. Smith (*ib.*, 19, 350, 1880) says 1 in 80,000,000. A. Ebeling (*Zeit. öffent. Chem.*, 8, 144, 1901) adds potassium thiocyanate to the solution under reduction; J. Volhard (*Zeit. angew. Chem.*, 14, 609, 1901) says Ebeling's method is not trustworthy, because (1) nascent hydrogen reduces the thiocyanate and leads to low results; (2) any excess of thiocyanate leads to an increased consumption of the permanganate.

[3] According to M. M. P. Muir (*Chem. News*, 97, 50, 1908), the addition of 100 c.c. of a saturated solution of mercuric sulphate stops the reaction. MERCURIC SULPHATE SOLUTION.— Mix 20 grms. of mercuric sulphate with 8 c.c. of concentrated sulphuric acid, and stir up the pasty mass with 80 c.c. of water. If a yellow precipitate separates, add more sulphuric acid. Note the danger suggested by Mitscherlich, page 170.

[4] The solution reduces more quickly apparently owing to the catalytic action of titanic oxide.

[5] See page 181. G. Scagliarini and P. Pratesi (*Ann. Chim. applicata*, 19, 85, 1929) have shown that if the reduction is effected by metallic copper, none of the tetravalent titanium is reduced.

[6] F. O. von der Pfordten, *Liebig's Ann.*, 234, 257, 1886; 237, 201, 1887; F. Pisani, *Compt. rend.*, 59, 289, 1864; A. Gemmel, *Analyst*, 35, 198, 1910; C. Marignac, *Zeit. anal. Chem.*, 7, 112, 1868; E. Wiegand, *ib.*, 21, 510, 1882; H. A. Wells and W. L. Mitchell, *Journ. Amer. Chem. Soc.*, 17, 78, 1895; G. Gallo, *Atti Accad. Lincei*, (5), 16, i., 525, 1907; H. D. Newton, *Amer. J. Science*, (4), 25, 130, 1908; *Chem. News*, 98, 134, 1908; F. W. Hinrichsen, *Chem. Ztg.*, 31, 738, 1907; E. Knecht and E. Hibbert, *Analyst*, 36, 96, 1911.

[7] "More or less" because, while acid solutions of ferrous sulphate oxidise slowly on exposure to air, titanous sulphate oxidises very quickly, and this oxidation is the principal difficulty in the volumetric determination of titanium by this reaction.

more than that actually present.   This is a serious matter.[1]   If, therefore, the zinc reduction be adopted, the titanium should be re-oxidised by adding a little bismuth oxide to the reduced solution.   According to Gooch and Newton,[2] this treatment will oxidise the Ti_2O_3 without affecting the ferrous salt.   The reduced solution should be filtered in order to remove the unreduced bismuth oxide and bismuth.   In illustration of the effect of bismuth oxide, Gooch and Newton quote the following test experiments:—

Table XXIX.—*Effect of Bismuth Oxide in Inhibiting the Effect of Titanium in the Permanganate Process for Iron.*

Grm. TiO_2 taken.	Grm. Fe_2O_3 taken.	Grm. Fe_2O_3 found.	Error.
0·04	0·0993	0·0992	– 0·0001
0·06	0·0993	0·0993	0·0000
0·08	0·0993	0·0997	+0·0004
0·1	0·0993	0·0997	+ 0·0004
0·2	0·0993	0·0997	+ 0·0004
0·1	0·1986	0·1986	0·0000

It is difficult to filter a ferrous solution without re-oxidation of a portion of the ferrous salt; the addition of ammonium sulphate retards re-oxidation.[3]   A filtration flask is fitted with a glass filter tube which has a sintered glass disc fused into it.   A couple of fragments of magnesite (iron-free) are placed in the filtration flask along with about 2 c.c. of dilute sulphuric acid; another couple of fragments of magnesite are placed in the filter tube, and also in the flask containing the reduced solution.   The filter flask is connected with the pump, and the reduced solution is poured into the filter tube.   The empty flask is now washed out with dilute sulphuric acid.   In this way, an atmosphere of carbon dioxide may be kept between the solution containing the reduced iron and the atmosphere.[4]   The solution in the filtration flask can then be titrated with permanganate without interference from the titanium.

The Reductor.-- The apparatus suggested by Jones [5] can be used for rapid zinc reductions.   A modification is illustrated in fig. 69.   A piece of glass tubing—40 to 45 cm. long and 12 to 15 mm. internal diameter—is drawn out

[1] For the effect of vanadium, see pages 518 and 536.

[2] F. A. Gooch and H. D. Newton, *Amer. J. Science*, (4), **23**, 365, 1907; *Zeit. anorg. Chem.*, **54**, 213, 1907; *Chem. News*, **96**, 148, 1907; H. D. Newton, *ib.*, **98**, 218, 1908; *Amer. J. Science*, (4), **25**, 343, 1908; R. Rieke and R. Betzel, *Sprech. Archiv*, **1**, 45, 1912.   For copper sulphate and copper oxide instead of bismuth oxide, see W. C. Birch, *Chem. News*, **99**, 272, 1909; A. Storch, *Ber. Oester. Ges. Förder. Chem. Ind.*, **15**, 9, 1893.   W. M. Thornton, jun., R. Roseman and S. I. Katzoff (*Journ. Amer. Chem. Soc.*, **54**, 2131, 1932) claim that by bubbling air through the reduced solution negligble quantities of ferrous iron are oxidised in the time needed to re-oxidise the trivalent titanium.   See also W. M. Thornton, jun., and R. Roseman, *ib.*, **57**, 619, 1935.

[3] A. Leclèrc, *Journ. Pharm. Chim.*, (7), **7**, 587, 1913.   Acid and neutral solutions of ferrous salts do not oxidise rapidly at ordinary temperatures, but more quickly if the liquid be warm.   Alkaline solutions oxidise quickly—C. Baskerville and R. Stevenson, *Journ. Amer. Chem. Soc.*, **33**, 1104, 1911.

[4] For more elaborate schemes, see W. Bachmeyer, *Zeit. anal. Chem.*, **24**, 59, 1885; N. von Klobukow, *ib.*, **24**, 395, 1885.

[5] D. J. Carnegie, *Journ. Chem. Soc.*, **53**, 468, 1889; C. Jones, *Trans. Amer. Inst. Min. Eng.*, **17**, 414, 1888–9; *Chem. News*, **60**, 93, 1889; P. W. Shimer, *Journ. Amer. Chem. Soc.*, **21**, 723, 1899; E. H. Miller and H. Frank, *ib.*, **25**, 919, 1903; D. L. Randall, *ib.*, **28**, 389, 1906; *Amer. J. Science*, (4), **24**, 313, 1907; *Chem. News*, **97**, 113, 1908; C. B. Dudley and F. N. Pease, *Journ. Anal. App. Chem.*, **7**, 108, 1893; F. L. Crobough, *ib.*, **6**, 366, 1892.

at one end, and there fitted into the neck of a filtration flask by means of a one-hole rubber stopper. The other end of the tube is fused to a stoppered cylindrical funnel. Put a filter plate or a few pieces of broken glass into the lower portion of the funnel, then about 2½ cm. of coarse, clean, calcined quartz sand. Fill the funnel with about 200 to 300 grms. of amalgamated or ordinary zinc powder[1] granulated to pass a 20's lawn, and remain on a 30's lawn. The zinc should be as free from iron as possible.[2] To use the apparatus, close the stopcock; pour 100 c.c. of cold dilute sulphuric acid (1 : 20) into the funnel. Apply suction at the filtration flask, since the hydrogen evolved retards the percolation of the acid through the tube. Open the stopcock to allow the acid to pass slowly through the column of granulated zinc. Wash the zinc free from acid with about five rinsings of distilled water. Repeat the treatment with acid and water. Close the stopcock so that the tube remains full of water. Disconnect the filtration flask, wash and restore it to its place. The tube is now ready for use.

Pour the iron solution[3] to be reduced into the funnel. Connect the filtration flask with the pump. Open the stopcock cautiously, since the

FIG. 69.—Reductor.

rate of flow of the solution to be reduced is regulated by the stopcock. As the solution flows through the column of zinc, complete reduction occurs, and

[1] The use of amalgamated zinc (proposed by A. J. McKenna) in place of ordinary zinc, enables a shorter reductor to be used. This is due to the more vigorous action of the amalgamated zinc. G. F. Smith and J. Rich (*Journ. Chem. Educn.*, 7, 2948, 1930) use an amalgamated zinc wire, 3 mm. in diameter, coiled into a spiral, in place of a reductor, especially for iron determinations. Reduction is complete in 30 minutes in the presence of 6 to 10 per cent. by volume of concentrated sulphuric acid. For a summary of metals for use in reductors, see G. F. Smith and C. S. Wilcox, *Ind. Eng. Chem. Anal. Ed.*, 9, 419, 1937.

[2] Commercial zinc dust is generally less pure than the granulated metal. It contains cadmium, lead and zinc oxide, together with iron. Zinc, at 210°, is very brittle, and it can be easily reduced to fine grains by trituration at this temperature—T. M. Brown, *Iron*, 12, 361, 1878; *Dingler's Journ.*, 228, 378, 1879. Zinc granules of 10's to 20's mesh size are useful.

[3] The ratio of free sulphuric acid (sp. gr. 1·84) to the total solution should be between 1 : 5 and 1 : 7, *i.e.* about 15 c.c. of concentrated sulphuric acid per 100 c.c. of solution. If more acid be present than 1 : 5, zinc sulphate is inclined to crystallise in the reductor; and if less than 1 : 7 be present, the reduction may not be complete in the case of uranium solutions—E. F. Kern, *Journ. Amer. Chem. Soc.*, 23, 685, 1901; F. Ibbotson and S. G. Clark, *Chem. News*, 103, 146, 1911. A. A. Blair (*The Chemical Analysis of Iron*, Philadelphia, 92, 1908) used the reductor for phosphorus determination; F. A. Gooch and G. Edgar (*Chem. News*, 87, 265, 1903; *Amer. J. Science*, (4), 25, 233, 1908) for vanadium; G. Edgar (*ib.*, (4), 25, 332, 1908) for vanadium and molybdenum; E. F. Kern (*Journ. Amer. Chem. Soc.*, 23, 685, 1901; F. Ibbotson and S. G. Clark, *Chem. News*, 103, 146, 1911) for uranium; see phosphorus, page 678.

the solution collects in the filtration flask ready for titration or for treatment with bismuth oxide. Just before the funnel is emptied rinse round its sides, also rinse the empty beaker or flask with water and let the washings pass through the reductor.[1] Wash the column of zinc with distilled water as before. The reductor is then ready for another reduction.

The reductor should be tested from time to time with blank tests. A correction for the iron in the zinc can be made by re-reducing the solution used in the permanganate titration. The amalgamated zinc in the tube charged as indicated above will suffice for thirty to forty reductions.

Reduction by Ammonium Bisulphite.—Hydrogen sulphide, sulphur dioxide, ammonium bisulphite, or sodium sulphite can be used for reducing the iron. These agents have the advantage of leaving the titanic oxide unaffected. Ammonium bisulphite, recommended by Austen and Hurff,[2] is convenient. It can be either made or purchased.[3] The solution under investigation is concentrated by evaporation to 40 or 50 c.c. Gradually add about 10 c.c. of dilute sulphuric acid (1 : 1) to the solution in an Erlenmeyer's flask, so as to make the solution distinctly acid.[4] Add a concentrated solution of ammonium bisulphite[5] and agitate the mixture thoroughly; or pass a current of sulphur dioxide through the acid solution. Gradually raise the temperature of the solution to boiling, and when a drop no longer gives a brownish-red coloration with ammonium thiocyanate, the ferric oxide is all reduced.

To remove the excess of sulphurous acid, place the flask on a sheet of asbestos on a tripod. Add 15 c.c. of dilute sulphuric acid (1 : 1). Cover the flask with the perforated lid of a Rose's crucible.[6] Pass a current of carbon dioxide at the rate of 3 or 4 bubbles per second through the solution.[7] The delivery tube passes through the hole in the cover of the flask. Meanwhile the flask is heated to the boiling-point of the solution. The velocity of the carbon dioxide is then reduced to about 1 bubble per second. After 20 or 30 minutes' boiling, the escaping steam will probably be free from sulphur dioxide, as shown by its failure to discolour a mercurous nitrate test paper.[8]

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[1] In washing the reductor free from iron the water should be kept above the level of the zinc, to prevent any air spaces forming between the successive additions of water. There is otherwise a possible formation of hydrogen peroxide which might spoil the results.

[2] P. T. Austen and G. B. Hurff, *Chem. News*, 46, 287, 1882; *Amer. Chem. Journ.*, 4, 282, 1882; T. W. Hogg, *Chem. News*, 59, 207, 1889; R. W. Atkinson, *ib.*, 49, 217, 1884. According to B. Glasmann (*Zeit. anal. Chem.*, 43, 506, 1904), the ammonium bisulphite does not reduce chromic salts and hence the presence of chromium does not interfere.

[3] AMMONIUM BISULPHITE.—Pass sulphur dioxide into a concentrated solution of ammonia until the solution becomes yellow and smells strongly of sulphur dioxide. If the solution be kept cool during the passage of the gas, white crystals of the normal sulphite are formed. These are gradually dissolved by the excess of sulphur dioxide, and the solution becomes clear yellow. Sulphur dioxide is best purchased in syphons of the liquefied gas. The syphons are a convenient source of the gas for analytical work.

[4] The reduction of ferric solutions by sulphur dioxide proceeds rapidly if the solution contains a little free acid, but not if the solution is alkaline to litmus—A. C. Cumming and E. W. Hamilton, *Proc. Roy. Soc. Edin.*, 32, 12, 1912.

[5] 1 c.c. of the solution per 0·5 grm. of Fe_2O_3.

[6] Or bend down the corners of a piece of platinum foil with two holes: one hole permits the escape of steam and gas; the other is for the gas delivery tube.

[7] The carbon dioxide is purified by passing it through a column of pumice soaked in copper sulphate and a water wash-bottle.

[8] MERCUROUS NITRATE TEST PAPER.—The paper is made by soaking No. 00 Swedish filter-paper in a solution of mercurous nitrate (0·5 to 5 per cent.) and drying. The paper is cut in strips and preserved for use in dry glass tubes, corked and sealed. H. Jervis (*Chem. News*, 77, 133, 1898) closes the flask with a stopper fitted with a delivery tube, one end of which dips into a very dilute acid solution of permanganate. If the solution be completely decolorised (without a brown precipitate), sulphur dioxide is still being evolved—H. Schiff, *Liebig's Ann.*, 118, 91, 1861.

In that case, place the flask in a dish of cold water to cool, while the current of carbon dioxide still bubbles through the solution—1 bubble per second.[1] When cold, the contents of the flask can be titrated with a standard solution of potassium permanganate, as indicated below. The titanium oxide is not reduced by the treatment with ammonium bisulphite.

§ 84. The Standardisation and Use of Potassium Permanganate Solution.

The "commercially pure" potassium permanganate picks up dust, etc., and is rather poorer in oxygen than theory requires,[2] although, by repeated crystallisation from boiling water and careful drying, the salt can be prepared to give a solution of exactly theoretical strength.[3] It is, however, the invariable custom to find the strength of, that is, to standardise, the solution of potassium permanganate.

Standard Solution of Sodium Oxalate.—Dissolve 0·42 to 0·43 grm. of potassium permanganate ($KMnO_4$, molecular weight 158·03) in a litre of water, and let the solution stand two or three weeks in order that the permanganate may oxidise any impurities in the water before the solution is standardised by titration with, say, a solution of sodium oxalate of known strength. Other substances[4] are in common use, but sodium oxalate gives exact results with very little trouble. Whatever substance be selected, the standard solution must be made up with the greatest care, since all the subsequent results depend upon the accuracy of the work at this stage. Sörensen's sodium oxalate[5] ($Na_2C_2O_4$, molecular weight 134) is the best "brand" for the purpose. This

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[1] As a matter of fact, it is rather difficult to remove the last trace of sulphur dioxide, and if all be not removed the iron determination will be high. The condensation of water in the neck of the flask and on the stopper is the main source of the trouble, for the condensed water absorbs some sulphur dioxide and, on dropping back into the solution, returns some sulphur dioxide. For the retention of sulphur dioxide by rubber stoppers and rubber tubing, see E. W. Hamburger, *Zeit. physiol. Chem.*, **2**, 191, 1878; **4**, 249, 1880; K. H. Huppert, *ib.*, **17**, 87, 1893.

[2] According to F. Raschig (*Zeit. angew. Chem.*, **16**, 585, 1904), a solution prepared from commercial permanganate was about 0·8 per cent. too weak.

[3] W. M. Gardner, B. North and A. R. Naylor, *Journ. Soc. Chem. Ind.*, **22**, 731, 1903.

[4] W. D. Treadwell and H. Johner (*Helv. Chim. Acta*, **7**, 528, 1924) recommend sublimed anhydrous oxalic acid, or the hydrated acid dried by air previously passed over a mixture of the anhydrous and hydrated acid. N. Schoorl (*Chem. Weekb.*, **25**, 73, 1928) frees oxalic acid from vacuole water by pulverisation and air drying, or by dehydration at 60° and regeneration by atmospheric moisture during a few days. I. M. Kolthoff and J. C. van Dijk (*Pharm. Weekblad*, **61**, 561, 1924; I. M. Kolthoff, *Zeit. anal. Chem.*, **64**, 185, 255, 1924) say that pure ferrous ammonium sulphate is a better agent than oxalic acid for standardising permanganate solutions. L. Moser and W. Schöninger (*Zeit. anal. Chem.*, **70**, 235, 1927) describe the preparation and use of electrolytic iron as a standard, and J. A. N. Friend and E. G. K. Pritchett (*Journ. Chem. Soc.*, 3227, 1928) that of ferrous sulphate. M. M. Kirilov (*Journ. App. Chem.* (U.S.S.R.), **9**, 2065, 1936) uses anhydrous ammonium oxalate.

[5] S. P. L. Sörensen, *Zeit. anal. Chem.*, **36**, 639, 1897; **42**, 333, 512, 1903; **44**, 141, 1905; S. P. L. Sörensen and A. C. Andersen, *ib.*, **44**, 156, 1905; L. Vanino and E. Seitter, *ib.*, **41**, 141, 1902; A. Skrabal, *ib.*, **42**, 359, 1903; C. Meineke, *ib.*, **39**, 322, 1900; S. P. L. Sörensen (*Compt. rend.*, 6e Conférence internat. Chim. (Bucarest), 305, 1925), gives detailed directions for determining water, sodium carbonate and sodium bicarbonate in sodium oxalate. See also A. Kling and A. Lassieur, *ib.*, 288, 1925; C. del Fresno, *Zeit. Elektrochem.*, **31**, 199, 1925; G. Lunge, *Zeit. angew. Chem.*, **17**, 230, 269, 1904; **18**, 1520, 1905; F. Dupré and E. Müller, *ib.*, **15**, 1244, 1902; F. Dupré, *ib.*, **17**, 815, 1904; F. Dupré and A. von Küpffer, *ib.*, **15**, 352, 1902; W. Schranz, *Bull. Soc. chim.*, (3), **18**, 89, 1899; H. Kinder, *Chem. Ztg.*, **30**, 631, 814, 1906; **31**, 69, 1907; P. Lehnkering, *ib.*, **30**, 723, 1906; H. von Jüptner, *Oester. Zeit. Berg. Hütt.*, **44**, 14, 1896; R. S. McBride, *Journ. Amer. Chem. Soc.*, **34**, 393, 1912; *Circ. Bur. Standards*, **40**, 3, 1912; W. Pawloff, *Journ. Russ. Phys. Chem. Soc.*, **28**, 621, 1897; E. Moyer, *Chemist-Analyst*, **13**, 7, 1915.

salt is dried in an air oven at about 200° and cooled in a desiccator over calcium chloride. Transfer exactly 0·8392 grm. of the salt to a litre flask. Dissolve the salt in a little water and make the solution up to the litre mark. One cubic centimetre will be equivalent to 0·0003959 grm. of $KMnO_4$, or to 0·001 grm. of Fe_2O_3. This solution can be used for standardising the permanganate. The equivalents of other substances can easily be expressed in terms of sodium oxalate by means of the following table of conversions:—

Table XXX.—Conversion Table for Permanganate Solutions.

Substance.	Fe.	FeO.	Fe_2O_3.	$KMnO_4$.	$K_2Cr_2O_7$.	$Na_2C_2O_4$.	$H_2C_2O_4$.	$FeSO_4$ $(NH_4)_2$ SO_4 $6H_2O$.
Iron	1·00000	1·28653	1·42977	0·56607	0·87834	1·19983	0·80600	7·02257
Potassium permanganate	1·76656	2·27274	2·52582	1·00000	1·55157	2·11957	1·42387	12·04583
Potassium dichromate	1·11385	1·46480	1·62785	0·64450	1·00000	1·36603	0·91766	7·99528
Sodium oxalate	0·83345	1·07227	1·19165	0·47179	0·73205	1·00000	0·67177	5·85292
Oxalic acid	1·24073	1·59618	1·77392	0·70232	1·08972	1·48862	1·00000	8·71268
Ferrous ammonium sulphate	0·14240	0·18320	0·20360	0·07955	0·12508	0·17086	0·11467	1·00000

Standardisation of Potassium Permanganate with Sodium Oxalate.—Pipette 25 c.c. of the standard sodium oxalate solution into an Erlenmeyer's flask and add 20 c.c. of dilute sulphuric acid (1 : 4). Warm the solution to between 60° and 70° in order to hasten the subsequent action and then place the flask under a burette, with a glass tap, which has been filled with the permanganate solution to be standardised. Run the permanganate from the burette into the flask, and keep the contents of the flask in a state of rotary agitation while the permanganate is being added. When the colour of the permanganate begins to be discharged slowly, add the permanganate very cautiously, drop by drop. If the solution cools appreciably during the titration, it should be warmed up again to 60°–70° as and when necessary. Any drops of permanganate adhering to the sides of the flask must be washed into the bulk of the liquid. When a drop of the permanganate produces a permanent pink blush throughout the liquid in the flask, the titration is finished. Read the burette to the nearest tenth c.c. Repeat the whole titration in triplicate and take the mean of the three readings.

In titrating hot liquids, there is a danger of heating the burette and its contents. In such cases, burettes with a delivery jet at the side are recommended. Koninck's burette [1] is an ordinary burette with a ⌐-shaped jet. The idea is to prevent clouding the burette with condensed steam, and the heating of the liquid in the burette, which would cause an expansion of the contained solution.

Let n denote the mean number of cubic centimetres of the permanganate solution needed for the titration of the 25 c.c. of sodium oxalate solution. The reaction is symbolised:

$$5Na_2C_2O_4 + 2KMnO_4 + 8H_2SO_4 = K_2SO_4 + 5Na_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$$

[1] L. L. de Koninck, *Zeit. angew. Chem.*, 1, 187, 1888.

Since 1000 c.c. of the sodium oxalate solution are equivalent to 0·3959 grm. of $KMnO_4$, 25 c.c. will be equivalent to 0·3959 ÷ 40 grm. of $KMnO_4$. Hence, n c.c. of the permanganate solution has the equivalent of 0·3959 ÷ 40 grm. $KMnO_4$, and this is equivalent to 0·025 grm. of Fe_2O_3. Or, 1 c.c. of the permanganate solution is equivalent to 0·025 ÷ n grm. Fe_2O_3. The error with careful work is about one part in a thousand.[1]

Influence of Acids.—Sulphuric acid is needed to decompose the oxalate, and in titrating with permanganate, free acid is also needed to keep the manganese oxides in solution. Otherwise, the brown precipitate which separates will obscure the end-point. Too much sulphuric acid may lead to high results, since concentrated sulphuric acid reduces potassium permanganate. This is illustrated by the following experiments,[2] with 20 c.c. of an acidified solution of ferrous sulphate containing the equivalent of 0·080 grm. Fe_2O_3, and with various proportions of sulphuric acid (1 : 4). The volume of the permanganate solution required with different quantities of the acid is indicated by the following numbers:—

H_2SO_4	0	10	20	25	40	50	c.c.
$KMnO_4$	17·89	17·85	17·89	18·07	18·20	18·62	c.c.

To show that the increased consumption of permanganate was not due to impurities in the sulphuric acid, 150 c.c. of water and 50 c.c. of the same sulphuric acid were added to another 50 c.c. of the ferrous solution. The consumption of permanganate was practically the same as when a solution of the ferrous salt diluted with water only was used.

Hydrochloric acid is inadmissible because some permanganate is used in a side reaction, possibly: $16HCl + 2KMnO_4 = 5Cl_2 + 2MnCl_2 + 2KCl + 8H_2O$, which proceeds slowly in dilute solutions, but is accelerated by the presence of iron salts. Similar experiments to those indicated in the last paragraph were made with hydrochloric acid (sp. gr. 1·13). The results were:

HCl	0	5	10	15	20	30	c.c.
$KMnO_4$	17·89	19·25	19·75	20·12	20·50	20·50	c.c.

The side reaction is inhibited by the addition of manganese sulphate, as indicated on page 498.[3]

Nitric acid should be absent, because it is reduced to nitrous acid by the zinc in the reduction of the ferric oxide, and nitrous acid reduces the permanganate.[4]

Standardisation of Potassium Permanganate with Metallic Iron.—It is nearly always advisable, if convenient, to standardise a volumetric solution against a solution similar to that which is going to be titrated. Hence, many prefer to standardise the permanganate solution for iron determinations against a solution containing a known amount of metallic iron dissolved in, say, sulphuric acid. The difficulty is with the iron. Perfectly pure iron is exceedingly difficult to procure. The trace of impurity present in most specimens of "pure" iron acts as a reducing agent on the permanganate. Even electrolytic

[1] For the preparation of 0·01N-solutions of potassium permanganate, see J. O. Halverson and O. Bergeim, *Journ. Ind. Eng. Chem.*, **10**, 119, 1918.

[2] E. Waitz, *Zeit. anal. Chem.*, **10**, 158, 1870; J. P. Blunt, *Chem. News*, 8, 54, 1863; F. A. Gooch and E. W. Danner, *Amer. Journ. Sci.*, (3), **44**, 301, 1892; F. Jones, *Journ. Chem. Soc.*, **33**, 95, 1878.

[3] O. L. Barneby, *Journ. Amer. Chem. Soc.*, **36**, 1429, 1914; P. Wagner, *Zeit. phys. Chem.*, **28**, 33, 1899; F. A. Gooch and C. A. Peters, *Zeit. anorg. Chem.*, **21**, 185, 1899; J. Brown, *ib.*, **44**, 145, 1905; **47**, 314, 1905; *Amer. Journ. Sci.*, (4), **19**, 31, 1905.

[4] A. Terreil, *Zeit. anal. Chem.*, **6**, 116, 1867. For the influence of fluorides on the permanganate titration, see O. L. Barneby, *Journ. Amer. Chem. Soc.*, **37**, 1481, 1915.

iron is not quite free from objection.[1] It is frequently assumed that iron
wire contains on an average 0·3 per cent. of impurities—the limits lie
usually between 0·1 and 0·4 per cent. The amount of iron actually weighed
out is accordingly multiplied by 0·997 in order to estimate the strength of the
solution. This procedure assumes that the impurities merely diminish the
amount of metal weighed out, but exert no reducing action on the per-
manganate. This assumption is not justified. The impurities are present
as carbides, sulphides, phosphides, silicides, etc., and these substances develop
hydrocarbons, hydrogen sulphide, hydrogen phosphide, etc., when the iron
wire is dissolved in sulphuric acid. These products are easily oxidised by
permanganate. The consequence is that more permanganate is used than
corresponds with the amount of iron in the wire, and the permanganate titre is
accordingly too low. An error ranging from 1 to 2 per cent. may be made
in standardising potassium permanganate by means of iron wire assumed to
represent pure iron, and the error is increased instead of diminished by assuming
that the wire contains less than its own weight of iron.[2]

Samples of "analysed" iron can be obtained, but these are not satisfactory
for standardising the permanganate unless their iron value has been determined
in terms of permanganate. This is done by using permanganate standardised
by electrolytic iron [3] or sodium oxalate. The iron wire is cleaned, if necessary,
with sandpaper to remove grease or oil, and dissolved in sulphuric acid at a
gentle heat in a 200 c.c. flask fitted with a guard tube (fig. 68), and from
which the air has been previously expelled by a stream of carbon dioxide.
The cold solution is titrated with permanganate, as previously described.
Satisfactory samples with a known permanganate titre can be purchased.[4]

Higher results are obtained if the solution is made on a water bath in a
flask fitted with a Bunsen's valve than if the iron be dissolved in a similar
flask kept for a long time "on the boil." In the former case, the solution
contains more of the impurities than in the latter case. Similarly, if the
dissolution be conducted in a flask through which a current of carbon dioxide
is passing, the results depend upon the duration of the boiling, and the speed
at which the carbon dioxide is passed. But if the carbon dioxide be passed
for a long time, the results are the same whether the iron be dissolved on the
water bath or at a boiling temperature.[5]

[1] C. F. Roberts, *Amer. J. Science*, (3), **48**, 290, 1894; *Chem. News*, **70**, 189, 1894; F. P.
Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, **2**, 499, 1911; A. Classen, *Zeit.
anal. Chem.*, **242**, 516, 1903; F. Mohr, *Lehrbuch der chemisch. analyt. Titriermethods*, Braun-
schweig, 215, 1896; A. Skrabel, *Zeit. anal. Chem.*, **42**, 395, 741, 1903; **43**, 97, 1904; G. Lunge,
Zeit. angew. Chem., **17**, 265, 1904; H. Theile and H. Deckert, *ib.*, **14**, 1233, 1901; F. Dupré,
ib., **17**, 815, 1904; S. Avery and B. Dale, *Ber.*, **32**, 64, 2233, 1899; H. Verwer and F. Groll,
ib., **32**, 806, 1899; H. Verwer, *Chem. Ztg.*, **25**, 792, 1901; H. Kinder, *ib.*, **31**, 69, 117, 1907;
L. Brandt, *ib.*, **32**, 812, 830, 840, 851, 1908; C. A. Kohn, F. J. Brislee and H. H. Froysell,
B. A. Rep., 174, 1900; L. Moyaux, *Rev. Univ. Mines*, (1), **25**, 148, 1869; H. Cantoni and
M. Basadonna, *Ann. Chim. anal.*, **9**, 365, 1904; A. Ledebur, *Stahl Eisen*, **22**, 1242, 1902;
H. Kinder, *ib.*, **30**, 411, 1910; L. Brandt, *ib.*, **30**, 1844, 1910; W. M. Gardner, B. North
and A. R. Naylor, *Journ. Soc. Chem. Ind.*, **22**, 731, 1903.
[2] J. R. M. Irby, *Chem. News*, **30**, 142, 1874; M. Berthelot, *Bull. Soc. chim.*, (2), **21**, 58, 1874.
[3] L. Moser and W. Schöninger, *Zeit. anal. Chem.*, **70**, 235, 1927.
[4] A. Müller, *Stahl Eisen*, **26**, 1477, 1906. Such a sample contained carbon, 0·027; silicon,
0·013; phosphorus, 0·034; copper, 0·024; manganese, 0·005; sulphur, 0·008—total impurities
0·111 per cent. The "iron value" of the sample in terms of permanganate was equivalent
to 99·91 per cent. metallic iron.
[5] J. A. N. Friend and E. G. K. Pritchett (*Journ. Chem. Soc.*, 3227, 1928) state that,
provided the composition of the iron be accurately known, results agreeing to 0·1 per cent.
with the sodium oxalate method can be obtained by dissolving up to 1·4 grm. of iron in
150 to 200 c.c. of 4N-sulphuric acid in a flask fitted with a vertical tube. Immediately the
iron has dissolved, the hot solution is cooled and diluted to a minimum volume of 250 c.c.

Suppose 1 grm. of "analysed" iron wire contains the equivalent of 0·9991 grm. iron so far as the permanganate solution is concerned, this amount of iron is equivalent to $0·9991 \times 1·4298 = 1·4285$ grms. of Fe_2O_3. If w grams of the sample of iron be taken, and n c.c. of permanganate are required for the titration, obviously, 1 c.c. of the permanganate is equivalent to $1·4285 \, w \div n$ grm. of ferric oxide.

However, the manipulations with Sörensen's sodium oxalate are a little easier than with metallic iron, and the results appear quite as satisfactory.[1]

Preservation of Permanganate Solutions.—These solutions should be stored in a dark glass bottle with a well-fitting, ungreased glass stopper, and protected from direct sunlight. Solutions containing suspended oxide are liable to lose strength, and this with increasing rapidity with the lapse of time owing to the increase in the quantity of the suspended oxide.[2] Solutions of permanganate, freed from suspended oxide by filtration through asbestos, may have a lower titre after filtration than before, since asbestos exerts a slight reducing action on solutions of potassium permanganate.[3] The solution will keep a long time if it be kept out of contact with organic matter, dust, etc.[4] For the best work the solution should be standardised about every two months, but after keeping through the summer for about nine months, a solution with a titre 1 c.c. $= 0·002576$ grm. Fe_2O_3 only changed to 1 c.c. $= 0·002522$ grm. Fe_2O_3—that is, about 2 per cent. The stock bottle should be shaken before use in order to remove any water condensed in the upper part of the bottle by distillation from below.[5]

Burettes for the Permanganate Titration.—Burettes with glass taps must be used. The solution of permanganate must not come in contact with organic matter from, say, rubber jets or the lubricant of the stopcock. To guard against the latter contingency, pure powdered graphite can be used as a lubricant, since permanganate solutions do not touch it at ordinary temperatures.

Burettes and other glass apparatus which have been used for permanganate solutions should be cleaned and rinsed immediately after use. Brown stains of manganese oxide can be removed by means of sulphurous acid.

Temperature Corrections.—It is necessary to allow for the effect of variations of temperature exceeding $\pm 2°$ or $\pm 3°$ from the standard. Assume that the solution is standardised at 15°; then, if the solution be less concentrated than $0·01N\text{-}KMnO_4$, the correction table for water, page 22, may be applied. If

[1] Note that if the permanganate titre of the iron wire be determined by standardisation with sodium oxalate, the use of the iron wire appears redundant.

[2] H. N. Morse, A. J. Hopkins and M. S. Walker, *Amer. Chem. Journ.*, 18, 401, 1896; H. N. Morse and C. L. Reese, *ib.*, 20, 521, 1898; *Chem. News*, 78, 77, 90, 1898. For the slow development of oxygen with dilute sulphuric acid solutions of potassium permanganate, see G. Blau and T. Wallis, *Liebig's Ann.*, 345, 261, 1906; F. A. Gooch and E. W. Danner, *Ber.*, 26, 267, 1893; W. Blum, *Journ. Amer. Chem. Soc.*, 34, 1379, 1912.

[3] P. A. Tscheihwile, *Journ. Russ. Phys. Chem. Soc.*, 42, 856, 1910.

[4] R. W. Oddy and J. B. Cohen, *Journ. Soc. Chem. Ind.*, 9, 17, 1890; W. M. Gardner and B. North, *ib.*, 23, 599, 1904; B. Collitt, *Pharm. Journ.*, (4), 27, 724, 1908; R. Luboldt, *Journ. prakt. Chem.*, (1), 77, 315, 1859; G. Bruhns, *Zentr. Zuckerind.*, 14, 968, 1906; H. von Jüptner, *Oester. Zeit. Berg. Hütt.*, 31, 502, 1883; C. Meineke and K. Schröder, *Zeit. öffent. Chem.*, 3, 5, 1897. R. Luboldt (*Journ. prakt. Chem.*, (1), 77, 315, 1859) kept solutions unchanged for about a year, as did B. Grützner (*Arch. Pharm.*, 231, 321, 1892), "provided the solutions be protected from dust." T. Kato (*Journ. Chem. Soc. Japan*, 48, 408, 1927; F. Simond, *Dingler's Journ.*, 248, 518, 1883) coats the store bottle with black paper or varnish on the outside in order to protect the contents from light.

[5] According to R. Luboldt (*Journ. prakt. Chem.*, (1), 77, 315, 1859), a standard solution of permanganate can be heated for half an hour at 100° without alteration, but if potash be present the solution is decomposed.

the solution be between 0·1N- and 0·01N-KMnO$_4$, the following table may be used:—[1]

Table XXXI.—*Temperature Corrections for Potassium Permanganate Solutions.*   (Standard temperature 15°.)

	0°	1°	2°	3°	4°	5°	6°	7°	8°	9°
0°	..	..	..	..	..	+0·6	+0·6	+0·5	+0·5	+0·5
10°	+0·4	+0·4	+0·3	+0·2	+0·1	0	-0·2	-0·3	-0·5	-0·6
20°	-0·8	-1·0	-1·2	-1·4	-1·6	-1·8	-2·0	-2·3	-2·5	-2·8

The method of using the table will be obvious from the examples on page 23.

Calculations.—The reaction between the permanganate and the ferrous salt is:

$$10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = K_2SO_4 + 5Fe_2(SO_4)_3 + 2MnSO_4 + 8H_2O$$

EXAMPLE.—The results of the permanganate titration will have been entered up somewhat as follows: 1 c.c. of the permanganate used represented 0·001510 grm. Fe$_2$O$_3$; 1 grm. of clay was treated; the reduction was complete after 10 grms. of zinc had been dissolved in the solution, and the solution required 13·84 c.c. of permanganate at 16°. In a blank experiment, 10 grms. of zinc dissolved in sulphuric acid required 0·51 c.c. of the permanganate solution. Hence, 13·84 − 0·51 = 13·33 c.c. represents the permanganate consumption by the ferrous iron in the gram of clay. This is equivalent to 13·33 × 0·00151 = 0·0201 grm. Fe$_2$O$_3$; or the clay has 2·01 per cent. of Fe$_2$O$_3$. There was no need to apply the temperature correction.[2]

§ 85. The Volumetric Determination of Iron—Marguerite's Permanganate Process.[3]

Starting with the solution reduced by the ammonium bisulphite through which carbon dioxide is passing (page 174), remove and wash the carbon dioxide delivery tube—inside and out—into the flask with recently boiled distilled water.[4]   Run in the standardised permanganate solution exactly as described in the preceding section, until a permanent pink blush is suffused throughout the liquid being titrated.[5]   If desired, an allowance can be made if the vanadium be afterwards determined.

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[1] The table may also be used for N-, 0·1N- and 0·01N-solutions of sodium chloride; 0·1N- and 0·01N-solutions of silver nitrate; ammonium thiocyanate (1000 c.c. equivalent to 10 grms. Ag). The table is based on the work of A. Schulze (*Zeit. anal. Chem.*, **22**, 167, 1882), and may be modified for standard temperatures of reference other than 15°.

[2] After the titration, the ferric oxide may be again reduced and the manganic oxide, if present, removed by filtration. The titration can thus be repeated until the volume of the liquid becomes unwieldy—B. Godwin, *Amer. J. Science*, (2), **50**, 249, 1870; *Chem. News*, **22**, 269, 1870.

[3] F. Marguerite, *Compt. rend.*, **22**, 587, 1846; *Ann. Chim. Phys.*, (3), **18**, 244, 1846; F. Scheidung, *Zeit. angew. Chem.*, **8**, 78, 1895.

[4] If the solution has been reduced with zinc, with or without the bismuth oxide treatment, proceed with the titration as indicated in the text. It must be added that particles of filter-paper may also reduce both permanganate and hot dichromate solutions, and thus lead to high results.—S. G. Simpson, *Journ. Ind. Eng. Chem.*, **13**, 1152, 1921. The filter-paper may get into the solution when the ammonia precipitate is dissolved in dilute acid, and titrated directly.

[5] The solution must not be too hot, or an excess of permanganate will be required. Some prefer to work with cold solutions; others with solutions between 60° and 70° (probably best —W. C. Bray, *Journ. Amer. Chem. Soc.*, **32**, 1204, 1910). Whatever be the temperature used, the conditions must be the same as those adopted in standardising the permanganate.

Errors.—The most frequent sources of error arise from the imperfect reduction of the ferric oxide and the deterioration of the permanganate. The latter difficulty is easily overcome by frequently standardising the permanganate; and the former by testing the solution for the presence of ferric iron before the reduction is stopped. Care must also be taken that no re-oxidation occurs before the titration. There is also a slight error due to the incomplete reduction of the permanganate, which was pointed out by Bray.[1] This occurs more particularly with low-temperature titrations, high acid concentration and with a large volume of dilute solution. The conditions here recommended give most favourable results.

In illustration of the effect of titanium on the iron determination and in illustration of the magnitude of the errors which may be expected in the iron determination both by the ammonium bisulphite and the zinc reductions, the following data were obtained with eight independent analyses on one sample of clay. One gram of clay was taken for each determination, and the bisulphate fusion was divided into two equal portions, one reduced with zinc and the other with ammonium bisulphite.

Table XXXII.—*Comparison of Zinc and Bisulphite Reductions in the Permanganate Process for Iron in Clays.*

Zinc reduction.		Ammonium bisulphite.	
c.c. $KMnO_4$.	Fe_2O_3.	c.c. $KMnO_4$.	Fe_2O_3.
6·92	0·0100	5·15	0·0078
6·85	0·0099	4·70	0·0069
6·84	0·0099	5·27	0·0079
6·32	0·0091	5·02	0·0076
6·61	0·0096	4·89	0·0073
6·09	0·0088	4·43	0·0068
6·49	0·0094	5·13	0·0077
6·19	0·0089	5·01	0·0075

The mean value for the ferric oxide with the zinc reduction is 0·0094, or 1·88 per cent., and with the bisulphite reduction, 0·0074, or 1·48 per cent., with a deviation of about ±0·06.[2]

The clay contained 1·2 per cent. of titanium. If the clay contains vanadium, the V_2O_5 will also be reduced by the zinc to V_2O_3; and to V_2O_4 by sulphur dioxide (and possibly by hydrogen sulphide). The reduced oxides will be oxidised to V_2O_5 during the permanganate titration. The vanadium is, however, usually present in such small quantities that its influence can be neglected; see page 518.

Correction with Very Dilute Solutions.—If the amount of iron be small, a 0·02N- or 0·01N-solution of permanganate may be used. An error may now creep into the work owing to the fact that a certain quantity of permanganate is required to impart a perceptible colour to pure acidulated water. In such cases the volume of permanganate solution needed to impart the desired pink

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[1] W. C. Bray, *Journ. Amer. Chem. Soc.*, **32**, 1204, 1910; F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, **2**, 498, 1911.

[2] The error is no greater, indeed less, if the whole of the sample be operated upon.

coloration to an equivalent volume of acidulated water must be determined, and the result deducted from the permanganate used in the titration.

The solution remaining after the permanganate titration can be used for the titanium determination, and afterwards for the determination of phosphorus.

§ 86. Titration of Ferric Iron with Titanous Chloride.— Knecht's Process.

An alternative method is to determine the ferric iron directly by reduction with a standard solution of titanous chloride.[1] The reaction is

$$TiCl_3 + FeCl_3 = TiCl_4 + FeCl_2$$

The advantages of this process are (1) no preliminary reduction of the iron to the ferrous state is necessary, whereby much time is saved; (2) no errors are introduced owing to under-reduction, or re-oxidation of the reduced solution; (3) titanic salts are not simultaneously reduced in the process, so that no correction need be made for titanium, if present. On the other hand, the titanous chloride solution must be re-standardised each time before use, since it is very readily oxidised. The standard type of apparatus needed for the titration is shown in fig. 70. About 125 c.c. of 15 per cent. titanous chloride solution are boiled for 1 to 2 minutes with 250 c.c. of concentrated hydrochloric acid in a flask.[2] After rapidly cooling, the solution is diluted to about 2·5 litres with cold, freshly boiled distilled water. The mixture is well shaken and transferred to the tubulated aspirator.[3]

The tube connecting the side arm of the burette to the tubulure of the aspirator contains a bead valve[4] in the rubber joint by means of which the burette can be refilled from time to time.

In order to keep a reducing atmosphere above the solutions in the burette and aspirator, the neck of the latter is closed by a two-holed rubber bung[5] through which glass tubes pass connecting the aspirator, on the one hand, to the open end of the burette, and on the other, to a hydrogen generator.[6] This latter consists of a tube constricted at its lower end to a narrow opening.

[1] E. Knecht, *Ber.*, **36**, 166, 1549, 1903; E. Knecht and E. Hibbert, *ib.*, **40**, 3819, 1907; E. Knecht and E. Hibbert, *Journ. Soc. Chem. Ind.*, **30**, 396, 1911; E. Knecht and E. Hibbert, *New Reduction Methods in Volumetric Analysis*, London, 1918; A. Monnier, *Ann. Chim. anal.*, **21**, 109, 1916; F. Mach and P. Lederle, *Landw. Versuchs.-Stat.*, **90**, 191, 1917; W. M. Thornton, junr., and J. E. Chapman, *Journ. Amer. Chem. Soc.*, **43**, 91, 1921; L. Brandt, *Chem. Ztg.*, **48**, 265, 270, 1924; E. Zintl and A. Rauch, *Zeit. anorg. Chem.*, **146**, 281, 1925; O. Hackl, *Zeit. anal. Chem.*, **66**, 401, 1925; W. G. Emmett, *Journ. Amer. Chem. Soc.*, **50**, 2059, 1927; P. S. Brallier, *Ind. Eng. Chem.*, **19**, 846, 1927; V. G. Chlopin and L. E. Kaufman, *Journ. Appl. Chem. U.S.S.R.*, **2**, 91, 1928; W. D. McFarlane, *Biochem. Journ.*, **26**, 1034, 1932; *Ind. Eng. Chem. Anal. Ed.*, **8**, 124, 1936; S. Kaneko and C. Nemoto, *Journ. Soc. Chem. Ind. Japan*, **35**, 348, 1932; A. R. Wood, *Journ. Soc. Glass Tech.*, **20**, 324, 1936.

[2] Commercial titanous chloride somtimes contains sulphides, which are eliminated as hydrogen sulphide on boiling. The concentrated acid prevents the formation of metatitanic acid, H_2TiO_3. For the preparation of iron-free titanous solutions, see R. Roseman and W. M. Thornton, junr., *Amer. Journ. Sci.*, (5), **20**, 14, 1930; *Chem. News*, **141**, 119, 1930; *Journ. Amer. Chem. Soc.*, **57**, 328, 1935.

[3] This solution will be about 0·05 normal. A sufficient volume should be made to fill the aspirator completely to the neck. Any deposit, forming on the glass parts of the apparatus, can be removed by washing with a one per cent. solution of hydrofluoric acid when the aspirator is refilled.

[4] Made by inserting a pear-shaped pellet of glass in the middle of the rubber tubing. No valve is needed if the burette is provided with a two-way stopcock.

[5] All bungs must be of rubber. They should be cleaned from time to time by rinsing in toluene to soften them.

[6] A small Kipp's apparatus can be used.

The tube is charged with granulated zinc and the upper end closed by a rubber bung through which passes the lead-in tube from the aspirator. The lower end of the tube is immersed in hydrochloric acid (1 : 1), contained in a glass bottle.

To remove the last traces of air from the apparatus, the bead valve is opened and the solution allowed to fill the burette and the tube above it as far as possible. The valve is then closed and the solution in the burette run to waste; hydrogen is now passed through the system for a few minutes by keeping the tap of the burette open.

Standardisation of the Solution.—Make an exactly 0·05N-solution of ferrous iron by dissolving 4·9017 grms. of the purest ferrous ammonium sulphate in 150 c.c. of cold, air-free distilled water; add about 15 c.c. of concentrated sulphuric acid (sp. gr. 1·84) and dilute to 250 c.c. in a graduated flask.[1] Pipette out 25 c.c. of this solution and oxidise it by running in an approximately 0·02N-permanganate solution until a faint pink colour persists. 10 c.c. of a 20 per cent. solution of potassium thiocyanate are then added and the mixture is titrated with the titanous chloride solution until the red colour of the ferric thiocyanate is just discharged. This titration gives directly the strength of the titanous chloride solution in terms of iron. Several litres of an approximately 0·05N-ferric iron solution are next made [2] and the exact iron value of the solution determined by titration against the standardised titanous chloride. This ferric solution is used as a secondary standard for the subsequent re-standardisations of the titanous chloride, thus avoiding the preparation and oxidation of a standard ferrous iron solution.
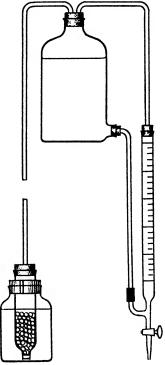
FIG. 70.—Titanous Chloride Titration Apparatus.

Titration with Titanous Sulphate.—Some chemists prefer to use a solution of titanous sulphate, as it is not nearly so sensitive to atmospheric oxidation as is the chloride and an open burette can be employed.[3] A solution of titanic sulphate in 4N-sulphuric acid is made of approximately the required normality and, when needed, a suitable volume of it is reduced by shaking

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[1] W. M. Thornton, jun., and A. E. Wood (*Ind. Eng. Chem.*, 19, 150, 1927) report that ferrous ammonium sulphate from different sources gives varying results. Hence they use an iron ore of accurately known iron content for the primary standard. E. Zintl and A. Rauch (*Zeit. anorg. Chem.*, 146, 281, 1925) standardise against pure copper sulphate. See E. Knecht and E. Hibbert, *New Reduction Methods in Volumetric Analysis*, London, 55, 1918.

[2] FERRIC IRON SOLUTION.—Dissolve 24 grms. of ammonium ferric alum, $(NH_4)_2SO_4.$ $Fe_2(SO_4)_3.24H_2O$, in 250 c.c. of water, add 60 c.c. of sulphuric acid (sp. gr. 1·84) and dilute to one litre.

[3] W. M. Thornton, junr., and J. E. Chapman, *Journ. Amer. Chem. Soc.*, 43, 91, 1921; W. M. Thornton, junr., *ib.*, 44, 998, 1922; A. S. Russell, *Journ. Chem. Soc.*, 497, 1926; W. M. Thornton, junr., and A. E. Wood, *Ind. Eng. Chem.*, 19, 150, 1927; H. Wilkinson and A. G. Tyler, *Journ. Soc. Dyers Col.*, 43, 114, 225, 1927; S. Kaneko and C. Nemoto, *Journ. Soc. Chem. Ind. Japan*, 35, 348, 1932.

for one minute with zinc amalgam.[1] The liquid is decanted into a flask, transferred to a burette and standardised immediately before use.[2]

§ 87. Determination of Iron with Ceric Sulphate—Lange's Process.

Although so far back as 1861 Lange recommended the use of ceric sulphate as a volumetric reagent, it is only since 1928 that this substance has found any extended application in analytical work.[3] Ceric sulphate dissolves in dilute acids to give an orange-coloured solution which has several advantages over potassium permanganate. For instance, (1) the solution is stable for months, provided reducing agents are excluded, and it is remarkably insensitive to external physical influences; (2) only one reduction product can be formed from ceric sulphate, namely, the cerous salt:

$$2Ce(SO_4)_2 + H_2 = Ce_2(SO_4)_3 + H_2SO_4$$

and (3) the reagent can be used in solutions containing a high concentration of hydrochloric acid.

Preparation of the Solution.—About 35 grms. of purified cerous oxalate are ignited in an iron crucible at $600°$-$625°$ with occasional stirring until the whole of the cerium present in the mixed oxides has been converted into ceric oxide.[4] The ignited oxides are then digested with sulphuric acid [5] (sp. gr. 1·5) at $125°$–$130°$ until dissolved. The solution is diluted and filtered, if necessary, from any insoluble residue and the filtrate made up to a litre to give an approximately 0·1 N-solution of ceric sulphate. Alternatively, 25 grms. of ceric nitrate are digested with concentrated sulphuric acid until the nitric acid has been completely expelled. The cooled solution is subsequently diluted to 500 c.c.[6]

Standardisation.—Willard and Young standardise by direct titration at $70°$ against a solution of sodium oxalate in dilute sulphuric acid.[7] As soon as an excess of ceric sulphate is present the solution acquires a yellow tinge. They found in a blank determination, made at $70°$ on 200 c.c. of water containing 20 c.c. of concentrated hydrochloric acid and 3-5 c.c. of concentrated sulphuric acid, that 0·05 c.c. of 0·1N-ceric sulphate was needed to give a pale

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[1] Heat 3 to 4 grms. of zinc with 100 grms. of mercury and some dilute sulphuric acid on a water bath for one hour. Well wash by decantation and separate the liquid amalgam from any solid residue. The amalgam can be used many times without loss of activity— T. Nakazono, *Journ. Chem. Soc. Japan*, **42**, 526, 1921.

[2] For the use of titanous chloride in the volumetric determination of copper, tin and chromium, see E. Knecht and E. Hibbert, *New Reduction Methods in Volumetric Analysis*, London, 1918.

[3] L. T. Lange, *Journ. prakt. Chem.*, (1), **82**, 129, 1861; F. L. Sonnenschein, *Ber.*, **3**, 631, 1870; G. Barbieri, *Chem. Ztg.*, **29**, 668, 1905; N. H. Furman, *Journ. Amer. Chem. Soc.*, **50**, 755, 1675, 1928; H. H. Willard and P. Young, *ib.*, **50**, 1322, 1334, 1928; **51**, 149, 1929; B. A. Soule, *ib.*, **51**, 2117, 1929; J. A. Atanasia and V. Stefavescu, *Ber.*, **61B**, 1343, 1928; R. Janssens, *Natuurwetensch. Tijds.*, **13**, 257, 1931; R. Vanossi and R. Ferramola, *Anales Asoc. Quim. Argentina*, **20**, 96, 1932; G. F. Smith, *et al.*, *Ind. Eng. Chem. Anal. Ed.*, **8**, 449, 1936.

[4] Ceric salts normally contain other rare earths. Ceric oxide can be purchased. The amount to be taken depends upon the purity of the sample; *e.g.* commercial ceric oxide contains about 40 per cent. CeO_2. The amount of cerous oxalate recommended here refers to a grade which will give a residual ceric oxide of about 85 per cent. purity. Very pure ceric oxide must be treated with concentrated sulphuric acid to obtain the sulphate and the resulting paste slowly poured into water. Ceric sulphate is also on the market.

[5] Sufficient sulphuric acid should be taken to give a solution which will be 1·0 N to 2·0 N with respect to this acid on dilution to a litre.

[6] A. J. Berry, *Analyst*, **54**, 461, 1929.

[7] A. J. Berry (*l.c.*) standardises against ferrous ammonium sulphate with **diphenylamine** as indicator.

yellow colour. Hence they recommend that a correction of -0.05 c.c. should be applied in every titration.

Determination of Ferrous Iron.—The iron in the acidified solution is suitably reduced and then titrated directly with the standardised ceric sulphate. Various indicators have been proposed. Willard and Young add to the reduced iron solution 15 c.c. of phosphoric acid solution [1] (sp. gr. 1.37) and 0.8 c.c. of a 0.1 per cent. solution of diphenylamine; [2] the colour change at the end-point is the same as that described in § 246, page 502. Mitchell and Ward use 0.5 c.c. of a 0.1 per cent. aqueous solution of Xylene cyanole FF; [3] a green colour is given, which changes very sharply to orange in the presence of excess of ceric sulphate. The colour change with both indicators is reversible, consequently over-titration can be corrected.[4]

§ 88. The Colorimetric Determination of Iron.

In 1853, Herapath [5] proposed to utilise the red colour produced when potassium or ammonium thiocyanate is mixed with a ferric salt for the determination of small quantities of iron.[6] According to Wagner,[7] this reaction enables 1 part of iron to be recognised in 1,600,000 parts of water. The

[1] Made by diluting phosphoric acid (sp. gr. 1.75) with an equal volume of water.

[2] See footnote 5, page 502, for details of preparation.

[3] A. D. Mitchell and A. M. Ward, *Modern Methods in Quantitative Chemical Analysis*, London, 16, 1932.

[4] For the use of Methyl red, Erio glaucine and Erio green as indicators, see N. H. Furman and J. H. Wallace, junr., *Journ. Amer. Chem. Soc.*, 52, 2347, 1930; for triphenylmethane derivatives, see R. Vanossi and R. Ferramola, *l.c.*; for *o*-phenanthroline, see G. H. Walden, junr., L. P. Hammett and R. P. Chapman, *Journ. Amer. Chem. Soc.*, 55, 2649, 1933; for Alphazurine G, see R. B. Whitmoyer, *Ind. Eng. Chem. Anal. Ed.*, 6, 268, 1934.

[5] T. J. Herapath, *Journ. Chem. Soc.*, 5, 27, 1852; A. Thomson, *ib.*, 47, 493, 1885; J. Davies, *Chem. News*, 8, 163, 1863; A. Zega, *Chem. Ztg.*, 17, 1564, 1893; F. Seiler and A. Verda, *ib.*, 26, 803, 1902; L. Lapicque, *Bull. Soc. chim.*, (3), 2, 295, 1890; (3), 8, 113, 1892; J. W. Leather, *Journ. Soc. Chem. Ind.*, 24, 385, 1905; A. Jolles, *Arch. Hygiene*, 13, 402, 1901; N. Damaskin, *Arbeit Pharm. Inst. Dorpat*, 7, 40, 1891; J. W. Mellor, *Trans. Cer. Soc.*, 8, 125, 1909; Hadank, *Sprech.*, 42, 445, 1909; T. T. Morrell, *Amer. Chem.*, 4, 287, 1874; H. P. T. Oerum, *Zeit. anal. Chem.*, 43, 147, 1904; A. Jolles, *ib.*, 43, 537, 1904; 44, 6, 1905; H. A. Daniel and H. J. Harper, *Journ. Assoc. Off. Agric. Chem.*, 17, 286, 1934; F. Mylius and B. Foerster, *Ber.*, 25, 675, 1892; E. R. Budden and H. Hardy, *Analyst*, 19, 169, 1894; W. B. Walker, *ib.*, 50, 279, 1925; E. R. Dovey, *ib.*, 43, 31, 1918; T. Matejka, *Chem. Listy*, 15, 8, 1921; R. Willstätter, *Ber.*, 53B, 1152, 1920; L. Szegoe and B. Cassoni, *Giorn. Chim. ind. appl.*, 15, 281, 1933.

[6] H. B. Pulsifer (*Journ. Amer. Chem. Soc.*, 26, 967, 1906) used the red colour of ferric acetylacetonate with excellent results; and A. Vogel (*N. Rep. Pharm.*, 25, 180, 1876; S. Pagliani, *Gazz. Chim. Ital.*, 9, 23, 1879; E. E. Smith, *Journ. Amer. Chem. Soc.*, 1, 335, 1879), the red colour of ferric salts with salicylic acid. F. Alten, W. Weiland and E. Hille (*Zeit. anorg. allgem. Chem.*, 215, 81, 1933) used thiosalicylic acid. For the use of aa'-dipyridyl, see F. Blau, *Monats.*, 19, 647, 1898; F. Feigl, P. Krumholz and H. Hamburg, *Zeit. anal. Chem.*, 90, 199, 1932; K. Scharrer, *Zeit. Pflanz. Düng. Bodenk.*, 33A, 336, 1934; W. D. MacFarlane, *Ind. Eng. Chem. Anal. Ed.*, 8, 124, 1936. For the colours with ammonium sulphide, and with potassium ferrocyanide, see J. W. Mellor, *Trans. Cer. Soc.*, 8, 125, 1909. For the detection and colorimetric determination of ferrous salts with 1 : 2-dioximes, *e.g.* dimethylglyoxime, see L. Tschugaeff and B. Orelkin, *Zeit. anorg. Chem.*, 89, 401, 1914; P. M. Koenig, *Chim. et Ind.*, 7, 55, 1922; E. J. Kraus, *Zeit. anal. Chem.*, 71, 189, 1927; for resorcylaldoxime, see S. L. Chien and T. M. Shih, *Journ. Chinese Chem. Soc.*, 5, 154, 1937; for *o*-phenanthroline, L. G. Saywell and B. B. Cunningham, *Ind. Eng. Chem.*, 9, 67, 1937; L. G. Saywell, *Fruit Products Journ.*, 16, 201, 1937; for 7-iodo-8-hydroxyquinoline, J. H. Yoe and R. T. Hall, *Journ. Amer. Chem. Soc.*, 59, 872, 1937; H. W. Swank and M. G. Mellon, *Ind. Eng. Chem. Anal. Ed.*, 9, 406, 1937.

[7] A. Wagner, *Zeit. anal. Chem.*, 20, 349, 1881. E. E. Smith (*ib.*, 19, 350, 1880) says 1 part in 8,000,000.

colour is due to the formation of a double salt—$Fe(CNS)_3 . 9KCNS . 4H_2O$.[1]   A large excess of potassium thiocyanate is needed to transform all the ferric salt into the thiocyanate and so produce the maximum coloration.[2]   The intensity of the coloration is proportional to the amount of ferric thiocyanate in solution; hence, if a given solution containing a known amount of iron has the same colour as a solution containing an unknown amount of iron, it is inferred that both solutions have the same concentration, as indicated in discussing the principles of colorimetry, page 72.

Unfortunately, the intensity of the coloration of solutions of ferric thiocyanate is very sensitive to the presence of other salts in the solution.[3]   In the case of dilute aqueous solutions the intensity of the coloration is not quite proportional to the amount of ferric iron present in the solution,[4] because some of the ferric thiocyanate is hydrolysed by the solvent: $Fe(CNS)_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCNS$.   Hence, when aqueous solutions are compared, the concentration of the solutions must be approximately the same.   With the pyrosulphate fusion, in silicate analyses, the solutions have so nearly the same composition that the error from this cause can be regarded as negligibly small. Consequently, when but small quantities of iron are in question—up to 5 per cent.—the determination can be made much more conveniently by the colorimetric process than by gravimetric or volumetric methods.

Test Solution.—The iron is here all in the ferric state; if otherwise, it would be necessary to oxidise the solution first.   Make the pyrosulphate fusion up to 250 c.c. with water.   Pipette 25 c.c. into a 250 c.c.[5] flask, and make the solution up to the mark with water to give the test solution.

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[1] G. Krüss and H. Moraht, *Liebig's Ann.*, 209, 98, 1889; *Zeit. anorg. Chem.*, 1, 399, 1893; A. Rosenheim and R. Cohn, *ib.*, 27, 295, 1901.

[2] J. H. Gladstone, *Phil. Trans.*, 145, 179, 1885; *Journ. Chem. Soc.*, 9, 54, 1856.

[3] J. Pelouse (*Ann. Chim. Phys.*, (1), 44, 214, 1830) has shown that organic acids reduce the red colour very rapidly; also oxalates, citrates, tartrates, acetates, iodates, arsenates, phosphates, fluorides and sulphates.   Barium, strontium and calcium chlorides exert a decolorising action (M. Vernon, *Chem. News*, 66, 177, 191, 202, 214, 1892; J. H. Gladstone, *ib.*, 67, 1, 1893; A. Dupré, *ib.*, 32, 15, 1875; A. J. Shilton, *ib.*, 50, 234, 1884; H. Werner, *Zeit. anal. Chem.*, 22, 44, 1883); also A. von Hedenström and E. Kunau, *Zeit. anal. Chem.*, 91, 17, 1932; alumina also retards the development of the colour (R. R. Tatlock, *Journ. Soc. Chem. Ind.*, 6, 276, 352, 1887); and generally, the colour obtained with a given proportion of iron depends upon the nature of the substances present in the same solution.

[4] J. Riban, *Bull. Soc. chim.*, (3), 6, 916, 1892; (3), 7, 199, 1892; G. Krüss and H. Moraht, *l.c.*; A. Rosenheim and A. Cohn, *Zeit. anorg. Chem.*, 27, 280, 1901; H. Schulze, *Chem. Ztg.*, 17, 2, 1893; H. Ley, *Zeit. phys. Chem.*, 30, 193, 1899; G. Magnanini, *ib.*, 8, 1, 1891; *Rend. R. Accad. Lincei*, 7, 104, 1891; P. N. van Eck, *Pharm. Weekb.*, 53, 1570, 1916; L. Andrews, *Proc. Iowa Acad. Sciences*, 1, 4, 1894; C. Féry and E. Tassilly, *Bull. Sci. Pharm.*, 19, 11, 1912; E. Tassilly, *Bull. Soc. chim.*, (4), 13, 34, 1913; O. Mayer, *Monit. Scient.*, (5), 3, 81, 1913; B. S. White, *Journ. Ind. Eng. Chem.*, 7, 1035, 1915; J. A. Schaeffer, *ib.*, 4, 659, 1912.   In order to eliminate the variable effects produced by the presence of other substances in the same solution, Tatlock (*l.c.*) proposed to compare the tints of the ethereal extract of the ferric thiocyanate, since J. Natanson (*Liebig's Ann.*, 130, 246, 1864; C. Claus, *ib.*, 99, 51, 1856; W. Skey, *Chem. News*, 16, 201, 324, 1867) has shown that, under these conditions, the reaction is more sensitive and less affected by the composition of the aqueous solution— G. Lunge, *Zeit. angew. Chem.*, 10, 3, 1896; H. von Keler and G. Lunge, *ib.*, 8, 669, 1894; A. Seyda, *Chem. Ztg.*, 22, 1086, 1898; H. Lachs and H. Friedenthal, *Biochem. Zeit.*, 32, 130, 1911.   For similar reasons, W. M'Kim Marriott and C. G. L. Wolf (*Journ. Biol. Chem.*, 1, 451, 1905; J. W. Gregory, *Proc. Chem. Soc.*, 23, 306, 1907) used acetone.   H. N. Stokes and J. R. Cain (*Bull. Bur. Standards*, 3, 115, 1907) and H. L. Smith and J. H. Cooke (*Analyst*, 51, 503, 1926), a mixture of ether and isoamyl alcohol—2: 5.   H. W. Winsor (*Ind. Eng. Chem. Anal. Ed.*, 9, 453, 1937) uses 2-methoxyethanol and reports that this solvent gives a colour 85 per cent. more intense than that given by water.   For the effect of ether containing peroxides, see H. von Keler and G. Lunge, *l.c.*, and H. N. Stokes and J. R. Cain, *l.c.*

[5] The dilutions must be modified to suit the iron content of the clay.   The colour of the sample in the crucible after the determination of the loss on ignition gives a rough indication

The Comparison.—5 c.c. of the standard ferric oxide solution [1] are diluted to 100 c.c. in a graduated flask, giving a solution containing 0·000005 grm. Fe_2O_3 per c.c. Part of this diluted solution is transferred to a burette reading to 0·1 c.c., while a similar burette is filled with distilled water. Two small specimen glasses, preferably with parallel sides (*e.g.* the test glasses of a colorimeter [2]), are filled with (*a*) a mixture of 10 c.c. of potassium thiocyanate solution [3] with 10 c.c. of the buffer solution of potassium aluminium sulphate [4] and (*b*) a mixture of 10 c.c. of potassium thiocyanate solution with 10 c.c. of the test solution.

The diluted standard iron solution is added drop by drop from the burette to solution (*a*) and an equivalent amount of water from the second burette to solution (*b*)—stirring the two solutions well after each addition—until the tints in the two test glasses are the same. The tints are viewed against a neutral background by light transmitted through the sides of the glasses, or a colorimeter may be used for comparison. If more than 6 or 8 c.c. of the standard ferric oxide solution are required the results will be inexact, because it is difficult to determine the changes of tint with concentrated solutions of ferric thiocyanate. In this case, the test solution was not sufficiently diluted, and another start must be made with a more dilute solution.

Calculations.—If w grms. of clay be taken for an analysis, then the 250 c.c. of solution obtained from the pyrosulphate fusion will contain all the ferric oxide from w grms. of the clay. Assume that v c.c. of the pyrosulphate solution are diluted to 250 c.c. to give the test solution, and that V c.c. of the diluted standard ferric oxide solution are required to give a match in colour with 10 c.c. of the test solution. Each c.c. of the diluted standard ferric oxide solution contains 0·000005 grm. Fe_2O_3. Hence V c.c. contain $V \times 0 \cdot 000005$ grm. Fe_2O_3. Consequently 10 c.c. of the test solution likewise contain $V \times 0 \cdot 000005$ grm. Fe_2O_3 and 250 c.c. of the test solution will contain $25 \times V \times 0 \cdot 000005$ grm. Fe_2O_3. But 250 c.c. of the test solution contain v c.c. of the original pyrosulphate solution, therefore 250 c.c. of the pyrosulphate solution, or w grms. of the clay, have $(250 \times 25 \times V \times 0 \cdot 000005)/v$ grm. Fe_2O_3. The percentage of ferric oxide in the clay is hence:—

$$(100 \times 250 \times 25 \times V \times 0 \cdot 000005)/v \times w = 3 \cdot 125 V/vw \text{ or } 25V/8vw$$

For 1 grm. of clay and a dilution of 25 c.c. of pyrosulphate solution to 250 c.c. this reduces to $V/8$.

It is well to take the mean of at least three determinations.

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of the requisite dilution. For white burning clays, make 25 c.c. up to 250 c.c. Cream-coloured calcined clays may require 10 c.c. diluted to 250 c.c. For red burning clays dilute 5 c.c. to 250 or 500 c.c.

[1] FERRIC OXIDE SOLUTION.—Dissolve 0·6040 grm. of pure ammonium ferric alum, $(NH_4)_2SO_4.Fe_2(SO_4)_3.24H_2O$, in water, add 5 c.c. of concentrated sulphuric acid, and, when cold, make the solution up to a litre. One c.c. of this solution represents 0·0001 grm. of Fe_2O_3. This solution will keep indefinitely, under conditions where more dilute solutions would hydrolyse and deposit a brown oxide on the glass. W. French, *Chem. News*, 60, 235, 1889; L. L. de Koninck, *Bull. Soc. chim.*, (3), 23, 261, 1909.

[2] Smaller cylinders may be used than those indicated for Weller's colorimeter, page 74. Cylinders with a square cross-section, 2·5 cm. side and 8 cm. high, are convenient.

[3] POTASSIUM THIOCYANATE SOLUTION.—Dissolve 97 grms. of the recrystallised salt, free from iron, in a litre of water. For potassium chloride impurity, see J. Hendrick, *Chem. News*, 63, 130, 1891.

[4] POTASSIUM ALUMINIUM SULPHATE SOLUTION.—Fuse 0·05 grm. of alumina, prepared by strongly igniting pure ammonium alum in a platinum dish, with 5 grms. of potassium pyrosulphate until all is dissolved. Treat the solution as indicated for the pyrosulphate fusion, page 166. When the solution is made up to a litre, the amount used here should be such as to make the concentration of the solution of potassium aluminium sulphate in the two test cylinders nearly the same.

§ 89. Colorimetric Determination with Thioglycollic Acid—Lyons' Process.

Ferric salts in a concentration greater than 1 in 100,000 give with thioglycollic acid, CH_2SH . COOH, a blue colour which fades as the iron is reduced to the ferrous state by excess of the reagent. On making the reduced solution alkaline, a colour develops which varies from pink to reddish-purple according to the concentration of the solution. Lyons [1] ascribes this colour to the formation of an intensely coloured ferrothioglycollate ion, $Fe(CH_2SCOO)_2^{--}$.

The test is best carried out at a dilution of about 1 in 500,000.[2] Five c.c. of the neutral or faintly acidic test solution are transferred to a test glass, one drop of thioglycollic acid is added followed by 0·5 c.c. of 0·88 sp. gr. ammonia solution. The colour is compared with that given by standards containing known amounts of iron. When a match in colour is obtained, the test and standard solutions are of equal concentrations, and the percentage of iron in the material under examination can be directly calculated. Nickel, cobalt, manganese and uranium interfere. When silver, mercury, tin, copper, cadmium, bismuth, zinc or magnesium is present in concentrations comparable with the concentration of the iron, three to four drops of thioglycollic acid should be used. In concentrations of 1 in 1000 or over these metals interfere. This method makes possible the colorimetric determination of both ferrous and ferric iron in a solution. The total iron is determined by the thioglycollic acid and the ferric iron alone in a separate portion of the solution by the thiocyanate process.

Kröhnke [3] has described a method whereby amounts of iron of the order of 0·01 mgrm. per litre can be determined colorimetrically by utilising the blue coloration produced when a chloroform solution of *iso*-nitrosoacetophenone is mixed with a solution of ferrous iron.

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[1] E. Lyons, *Journ. Amer. Chem. Soc.*, **49**, 1916, 1927; H. W. Swank and M. G. Mellon, *Ind. Eng. Chem. Anal. Ed.*, **10**, 7, 1938. Compare R. Andreasch, *Ber.*, **12**, 1390, 1879; J. P. Claësson, *ib.*, **14**, 411, 1881.

[2] That is, about twice the normal dilution used in the thiocyanate process.

[3] F. Kröhnke, *Gas und Wasserfach*, **70**, 510, 1927. For the determination of iron in glass sands, see G. E. F. Lundell and H. T. Knowles, *Journ. Amer. Cer. Soc.*, **11**, 119, 1928; N. E. Densem, *Journ. Soc. Glass Tech.*, **20**, 303, 1936; L. Springer, *ib.*, **20**, 319, 1936. For a review of recently published papers on the determination of iron, see M. Frommes, *Zeit. anal. Chem.*, **97**, 36, 1934.

CHAPTER XV.

THE DETERMINATION OF TITANIUM.

§ 90. Weller's Colorimetric Process.

SCHEERER [1] and Riley have emphasised the almost ubiquitous occurrence of titanium in silicate rocks. Clays rarely contain more than 4 per cent. of titanic oxide, and where this limit is not exceeded, the colorimetric process [2] is usually the most convenient, though gravimetric and volumetric methods are also available [3]—see pages 193 and 197.

A solution of titanium sulphate produces an orange-yellow colour when oxidised with hydrogen peroxide.[4] The intensity of the coloration depends upon the proportion of titanium present.[5] If, therefore, a solution containing a known amount of titanium has the same tint as another solution of equal thickness of liquid, it is assumed that both solutions contain the same proportion of titanium. Hydrogen peroxide is therefore added to the solution under investigation, and the standard solution, containing a known amount of titanium, is systematically diluted until both solutions have the same tint.[6]

The presence of fluorine leads to low results, because fluorine partially bleaches the yellow colour produced by hydrogen peroxide. For instance, with solutions containing 0·01 grm. of titanic oxide:

Hydrofluoric acid present . 0·00 0·00039 0·00194 0·0039 .grm.
Titanic oxide found . . 0·01 0·0093 0·0080 0·0068 grm.

Steiger [7] has proposed a colorimetric process for fluorine based on this property.

[1] T. Scheerer, *Liebig's Ann.*, **92**, 178, 1854; *Chem. News*, **1**, 143, 1860; E. Riley, *Journ. Chem. Soc.*, **12**, 13, 1860; L. Dieulafait, *Compt. rend.*, **93**, 804, 1881.

[2] Note, if the filtrate from the silica is treated with hydrogen sulphide, some titanium will be precipitated by the hydrogen sulphide.

[3] For a review of methods for the determination of titanium and zirconium, see J. W. Marden, *U.S. Bur. Mines Bull.*, **212**, viii, 281, 1923.

[4] H. Schönn, *Zeit. anal. Chem.*, **8**, 380, 1869; **9**, 41, 330, 1870; A. Piccini, *Atti R. Accad. Lincei*, (3), **6**, 180, 1882; *Gazz. Chim. Ital.*, **12**, 151, 1882; **13**, 57, 1883; **14**, 38, 1884; V. Lehner and W. G. Crawford (*Journ. Amer. Chem. Soc.*, **35**, 138, 1913) recommend thymol; H. J. H. Fenton (*Journ. Chem. Soc.*, **93**, 1064, 1908) dihydroxymaleic acid—page 519; M. Schenk (*Helv. Chim. Acta*, **19**, 1127, 1936) salicylic acid, in the absence of iron. It is sometimes stated that titanium compounds give a yellow colour with ether in the presence of alcohol. This only occurs when the ether contains organic peroxides. C. Baskerville and W. A. Hamor, *Journ. Ind. Eng. Chem.*, **3**, 378, 1911; A. Stähler, *Ber.*, **38**, 2619, 1905; A. Jorrisen, *Ann. Chim. anal.*, **8**, 201, 1903; *Journ. Pharm.*, Liège, **33**, 1903. R. Schwarz (*Zeit. anorg. allgem. Chem.*, **210**, 303, 1933) says that the colour is not due to pertitanic acid, $TiO_3.nH_2O$, but to the formation of a complex, $H_2[TiO_2(SO_4)_2]$.

[5] H. Ginsberg (*Zeit. anorg. allgem. Chem.*, **198**, 162, 1931; **209**, 105, 1932; **211**, 401, 1933; **226**, 57, 1935) states that with less than 0·3 mgm. TiO_2 per 100 c.c. the depth of colour is not proportional to the concentration.

[6] A. Weller, *Ber.*, **15**, 2599, 1882; C. Baskerville, *Journ. Soc. Chem. Ind.*, **19**, 419, 1900; J. Brakes, *ib.*, **20**, 23, 1901; H. M. Ullmann and J. W. Boyer, *Chem. Eng.*, **10**, 163, 1909; A. Gautier, *Chim.*, **1**, 177, 1910; *Rev. gén. Chim.*, **14**, 14, 1910; G. P. Pamfil, *Monit. Scient.*, (4), **24**, 643, 1911.

[7] T. B. Osborne, *Amer. J. Science*, (3), **30**, 329, 1885; *Chem. News*, **53**, 43, 1886; W. F. Hillebrand, *ib.*, **72**, 158, 1895; *Journ. Amer. Chem. Soc.*, **17**, 718, 1895; J. H. Walton, *ib.*,

The presence of phosphoric acid bleaches the colour and leads to low results.[1]   For instance, with solutions containing the same amount of titanium oxide, 0·01 grm.:

Phosphoric acid	0·00	0·13	0·26	0·52	0·78	1·04	1·30	grm.
Titanic oxide	0·0100	0·0090	0·0083	0·0074	0·0069	0·0066	0·0064	grm.

Potassium sulphate also weakens the tint produced by the titanium oxide, unless an excess of sulphuric acid be present.[2]   For instance, with 6 grms. of potassium sulphate in each of three solutions containing the same amounts of titanium and hydrogen peroxide, Merwin found:

H_2SO_4	.	.	.	.	0·4	2·9	8·0 c.c.
Bleaching	.	.	.	.	21	14	5 per cent.

From which it follows that, the greater the excess of sulphuric acid, the less the bleaching action.

Owing to the fact that the test solution obtained in the above analytical scheme contains the potassium sulphate used in the pyrosulphate fusion, an equivalent amount of potassium sulphate can be added to the standard solution in order that the comparison of tints can be made under similar conditions.   In the same way, if the test solution contains appreciable quantities of phosphoric acid, an equivalent amount of phosphoric acid can be added to the standard solution.

A solution of ammonium molybdate in nitric acid,[3] as well as uranium [4] and vanadium salts,[5] gives somewhat similar tints, and hence these salts and chromates [6] should be absent.   The influence of iron salts will be discussed later.

The colorimetric process works well with quantities of titania in clay up to about 4 per cent.   There is a wide range over which the process is accurate.   This ranges between concentrations represented by 0·0015 and 0·0200

29, 481, 1907; G. Steiger, *ib.*, 30, 219, 1908; H. E. Merwin, *Amer. J. Science*, (4), 28, 119, 1909; E. Jackson, *Chem. News*, 47, 157, 1883; L. Lévy, *Compt. rend.*, 105, 754, 1888; C. Reichard, *Chem. Ztg.*, 28, 16, 1904.

[1] F. G. Germuth (*Journ. Amer. Chem. Soc.*, 50, 1910, 1928) recommends the addition of 1 c.c. of 0·1 per cent. uranium acetate solution for every 0·0001 grm. TiO₂ present to counteract the bleaching influence of the phosphoric acid.   The effect is stated to be independent of the amount of phosphoric acid present.   S. N. Rozanov and V. A. Kazarinova (*Zeit. Pflanz. Düng. Bodenk*, 35A, 223, 1934) have adapted Weller's process to materials high in phosphorus pentoxide.

[2] According to G. Steiger (*l.c.*), sodium salts give too high results.

[3] H. Schönn, *Zeit. anal. Chem.*, 9, 41, 330, 1870; H. Bärwald, *Ber.*, 18, 1206, 1885; *Beiträge zur Kenntnis des Molybdäns*, Berlin, 1885; T. Fairley, *Journ. Chem. Soc.*, 31, 127, 1877; J. Aloy, *Bull. Soc. chim.*, (3), 27, 734, 1903; *Chem. News*, 87, 102, 1903; G. Denigès, *Bull. Soc. chim.*, (3), 7, 1892; J. Werthier, *Journ. prakt. Chem.*, (1), 83, 195, 1861; J. B. Cammerer, *Chem. Ztg.*, 15, 957, 1891; E. Péchard, *Compt. rend.*, 112, 720, 1891; 114, 1358, 1481, 1892; *Ann. Chim. Phys.*, (6), 28, 537, 1893; G. Möller, *Zeit. phys. Chem.*, 12, 555, 1893; W. Muthmann and W. Nagel, *Zeit. anorg. Chem.*, 17, 73, 1898; H. Dufet, *Zeit. Kryst.*, 22, 594, 1894; A. Fock, *ib.*, 22, 32, 1894.

[4] Uranium salts (T. Fairley, *Journ. Chem. Soc.*, 31, 127, 1877; *Chem. News*, 33, 237, 1876; *Bull. Soc. chim.*, (2), 27, 111, 1877) give a yellow colour with hydrogen peroxide; tungsten salts give a similar tint—J. B. Cammerer, *Chem. Ztg.*, 15, 957, 1891; A. Piccini, *Zeit. anorg. Chem.*, 1, 51, 1892; E. Péchard, *Compt. rend.*, 112, 720, 1891.   Columbium salts give a yellowish-green colour, so that the test for titanium is not reliable in the presence of columbium—R. D. Hall and E. F. Smith, *Journ. Amer. Chem. Soc.*, 27, 1369, 1905; C. W. Balke, *ib.*, 30, 1637, 1908.

[5] G. Werther, *Journ. prakt. Chem.*, (1), 83, 195, 1861; E. Jackson, *Chem. News*, 47, 157, 1883; A. Scheuer, *Zeit. anorg. Chem.*, 16, 284, 1898.

[6] L. C. A. Barreswil, *Ann. Chim. Phys.*, (3), 20, 364, 1847; *Journ. prakt. Chem.*, (1), 41, 393, 1847; H. Moissan, *Compt. rend.*, 97, 96, 1883.

grm. titanium per 100 c.c. According to Wells,[1] the change in concentration required to produce a perceptible difference in the intensity of the colour of two solutions is about 6·5 per cent. The error is greater with weaker solutions, although by increasing the thickness of the layer of liquid [2] satisfactory comparisons can be made with solutions containing less than 0·0015 grm. of titanium per 100 c.c. Solutions more concentrated than 0·0200 grm. per 100 c.c. are not suited for colorimetric work. With the exercise of the greatest care, the accuracy of the colorimetric process for titanium is about 2 per cent. If more than 4 per cent. of titanic oxide be present, the gravimetric or volumetric processes are more reliable. More accurate results are obtained with colours not too intense, as the eye is not so sensitive to the small differences of tint in concentrated solutions. Colours approximating a deep straw yellow give the best results. The left eye is usually rather more sensitive than the right eye. Better results are obtained after a little practice with test solutions of known strength. *Cf.* p. 76.

Preparation of the Test Solution.—Pipette 50 c.c. of the stock solution obtained from the pyrosulphate fusion into a 100 c.c. graduated flask, add to it 9 c.c. of concentrated sulphuric acid[3] and sufficient hydrogen peroxide[4] to oxidise all the titanium in the solution. In general, 5 to 10 c.c. of hydrogen peroxide (10 vols.) suffice for 0·5 to 2 per cent. of titanium oxide. Make the solution up to 100 c.c. with distilled water. Pour a part of this solution into a test glass or the left cylinder of the colorimeter.

Preparation of the Standard Solution.— Pipette 5 c.c. of the standard solution[5] of titanium sulphate, containing 1 grm. TiO_2 per litre, into a 100 c.c. flask; add 10 c.c. of hydrogen peroxide,[6] and make the solution up to 100 c.c.[7] Each

[1] R. C. Wells, *Journ. Amer. Chem. Soc.*, 33, 504, 1911.

[2] In colorimeters of the type of Duboscq's (page 73).

[3] The solution should contain between 15 and 17 per cent. of sulphuric acid—that is, 9 c.c. of acid per 100 c.c., otherwise the results may be low owing to the bleaching action of potassium sulphate. P. Faber, *Chem. Ztg.*, 31, 263, 1906; *Zeit. anal. Chem.*, 46, 277, 1907; F. P. Dunnington, *Journ. Amer. Chem. Soc.*, 13, 210, 1891.

[4] HYDROGEN PEROXIDE.—This must be free from all traces of fluorides and phosphoric acid. For the detection of phosphates in hydrogen peroxide, see J. Dalietos, *Zeit. anorg. allgem. Chem.*, 217, 346, 1934. Pure aqueous solutions of hydrogen peroxide can be purchased; they should preferably be stored in a cool, dark place, to minimise spontaneous decomposition. The solution keeps better if acidified with dilute sulphuric acid.

[5] STANDARD SOLUTION OF TITANIUM OXIDE.—Fuse 1 grm. of pure titanic oxide with 15–20 grms. of potassium pyrosulphate until all has dissolved. The cold cake is extracted with dilute sulphuric acid and 50 c.c. of the concentrated acid then added. The mixture is gently warmed on a water bath until the cake has completely dissolved, and then the solution is diluted to 1 litre. If the purity of the titanic oxide is suspect, make the solution up to, say, 900 c.c. Take 50 c.c., dilute with water, heat to boiling, and precipitate the titanium hydroxide by the addition of ammonia. Wash the precipitate with hot water until free from alkalies, ignite, blast and weigh. Duplicate determinations should be concordant. The solution is now diluted until it contains exactly 1 grm. of TiO_2 per litre. The solution should be kept in a bottle with a glass stopper coated with vaseline. Withdraw the amount needed for a determination by means of a pipette. Do not pour the solution from the bottle. See page 736 for an alternative process. W. M. Thornton, jun., and R. Roseman (*Amer. Journ. Sci.*, (5), 20, 14, 1930) use potassium titanium oxalate, $K_2TiO(C_2O_4)_2.2H_2O$, for the preparation of the colorimetric standard. The salt is mixed with ammonium sulphate, gradually heated with concentrated sulphuric acid and then boiled for a few minutes.

[6] Both solutions should always be freshly prepared for a test.

[7] As much potassium sulphate as is present in the test solution may be added to the flask before making up with water to 100 c.c. If m grms. of potassium pyrosulphate have been used for the fusion of the ammonia precipitate, the 250 c.c. of stock solution obtained from the fusion will contain 0·7m grm. of potassium sulphate or 0·14m grm. per 50 c.c. of solution. Hence, approximately 20 c.c. of a solution of potassium sulphate containing 7m grms. K_2SO_4 per litre will be needed. The same quantity of potassium sulphate is added per 100 c.c. of water from the burette.

cubic centimetre is then equivalent to 0·00005 grm. of TiO_2. Put 10 c.c. of this standard solution into another test glass or the right cylinder of the colorimeter, and 50 c.c. of water into a burette.[1] Add water to the diluted standard solution, with stirring, until its colour is the same as that of the test solution. Note the amount of water added.

Calculation.—Suppose that v c.c. of water have to be added to the 10 c.c. of diluted standard titanium solution to produce equality in tint. The 5 c.c. of the standard solution contains 0·005 grm. TiO_2; this is diluted to 100 c.c., consequently 10 c.c. of the diluted solution contains 0·0005 grm. TiO_2. Hence, the test solution contains the equivalent of 0·0005 grm. TiO_2 per $(10+v)$ c.c., therefore 100 c.c. of the same solution contains $(100 \times 0·0005)/(10+v)$ grm. TiO_2. But the 100 c.c. of test solution was made up from 50 c.c. of the stock solution from the pyrosulphate fusion, and as 250 c.c. of the stock solution contains all the titanium oxide from 1 grm. of clay, 50 c.c. of it represents 0·2 grm. of clay. Consequently the clay contains $(100 \times 0·0005 \times 100)/(10+v) \times 0·2 = 25/(10+v)$ per cent. of TiO_2. If w grms. of clay be taken for analysis, and if V c.c. of the stock solution be diluted to 100 c.c., the per cent. of TiO_2 becomes $1250/(10+v)Vw$.

Correction for Iron.—According to Faber, if much iron be present, the results may be too high, because the iron intensifies the colour of the test solution. Hillebrand deducts 0·02 per cent. from the final result for every 10 per cent. of iron oxide present.[2] Faber[3] recommends the addition of phosphoric acid to both the standard and the test solutions in order to neutralise the effect of iron. It is necessary to add the phosphoric acid to both solutions, because it weakens the yellow tint, and both solutions are then affected in the same way. 20 c.c. of phosphoric acid (sp. gr. 1·3) per 100 c.c. will usually suffice.

W. A. Noyes[4] adds an amount of ferric ammonium alum[5] to the standard approximately equivalent to the amount of ferric oxide in the test solution. To allow for the presence of iron, therefore, first make an approximate determination of the titanium in the clay. Let a denote the final volume in c.c. of the standard after dilution; b the number of c.c. of water used in diluting the standard; p the amount of iron in the test solution in terms of Fe_2O_3 per c.c. and x the amount of Fe_2O_3 to be added per c.c. of water used in diluting the standard in the final test. Hence, bx denotes the amount of ferric oxide in the water used for diluting the standard solution; and ap denotes the amount of ferric oxide in the a c.c. of the diluted standard solution. Consequently,

$$bx = ap; \text{ or, } x = ap/b \text{ } Fe_2O_3 \text{ grm. per c.c.}$$

The ferric oxide is added as ferric ammonium sulphate. Since 160 grms. of ferric oxide are equivalent to 964 grms. of ferric ammonium alum, every gram of ferric oxide corresponds with 6 grms. of ferric ammonium alum.

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[1] The test solution should have a paler tint than the standard before the latter is diluted from the burette. If the clay contained excessive amounts of TiO_2, it may be necessary to take only 25 or even 10 c.c. of the stock solution from the pyrosulphate fusion in making up the test solution, or the standard solution may be made more concentrated.

[2] W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, 700, 160, 1919.

[3] P. Faber, *Chem. Ztg.*, 31, 263, 1906; J. H. Walton, *Journ. Amer. Chem. Soc.*, 29, 481, 1907.

[4] W. A. Noyes, *Journ. Anal. App. Chem.*, 5, 39, 1891.

[5] STANDARD IRON SOLUTION.—Dissolve 30 grms. of ferric ammonium sulphate in 500 c.c. of water, add 100 c.c. of concentrated sulphuric acid and make the solution up to a litre. The solution may be standardised, if necessary, by titration (page 180). Ferrous salts may exert a bleaching action on the titanium colour.

Gautier [1] recommends making up a permanent set of standard comparison tints from methyl orange dissolved in water; as a matter of fact this method is somewhat risky. Lovibond's tintometer offers some advantages in making up a standard comparison scale; see page 75.

Results.—To show the deviations which might be expected in titanium determinations, the following results were obtained in eight independent determinations of titanium in one sample of clay:—

0·0120; 0·0125; 0·0125; 0·0113; 0·0114; 0·0126; 0·0125; 0·0113

with a mean value 0·0120, or 1·20 per cent. The deviations from the mean are approximately ±0·07.

§ 91. The Gravimetric Determination of Titanium— Gooch's Process.

Titanium can be separated from aluminium by the prolonged boiling of a slightly acid solution of the sulphates.[2] Thus, Lévy found the amount of hydrolysis (*cf.* page 162) in solutions containing titanium and aluminium sulphates partly "neutralised" with potassium hydroxide and boiled for six hours:—

Table XXXIII.—Effect of Sulphuric Acid on the Precipitation of Titanic Oxide.

Free H_2SO_4 per 100 c.c.	Titanic oxide.	
	Used.	Precipitated.
0·000 *	0·086	0·108
0·000	0·086	0·100
0·000	0·036	0·047
0·083	0·036	0·036
0·500	0·086	0·085
1·000	0·082	0·086
5·766	0·030	0·000

* Slight excess of potassium hydroxide.

These results clearly show that if too much sulphuric acid be present, the titanium will be but imperfectly precipitated, whereas if too little acid be present, some aluminium will be precipitated. Hence the adjustment of the acidity of the solution is so difficult that the process is not at all satisfactory for general work.[3] Gooch's [4] method is based upon the solubility of alumina and

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[1] A. Gautier, *Chim.*, 2, 2, 1911; *Rev. gén. Chim.*, 14, 16, 1911. 1 grm. of methyl orange is dissolved in 500 c.c. of water; 10 c.c. of this solution are diluted to 200 c.c.; and the solution is matched with solutions containing known amounts of titanium. The standards can afterwards be preserved, for, according to Gautier, they do not fade.

[2] Zirconium, if present, will be precipitated under similar conditions—O. Hauser, *Zeit. anorg. Chem.*, 45, 185, 1905; J. J. Berzelius, *Pogg. Ann.*, 4, 117, 1825; H. Rose, *ib.*, 83, 148, 1851.

[3] L. Lévy, *Journ. Pharm. Chem.*, (5), 16, 56, 1887; *Ann. Chim. Phys.*, (6), 25, 433, 1892; H. Pellet and C. Fribourg, *Ann. Agron.*, (2), 2, 20, 1905; P. Holland, *Chem. News*, 59, 27, 1889; D. Forbes, *ib.*, 19, 3, 1869; J. Brakes, *Journ. Soc. Chem. Ind.*, 18, 1097, 1899; C. Baskerville, *ib.*, 19, 419, 1900; P. Farup and E. Schreiner, *Tidschrift Kem. Farm. Terapi*, 11, 65, 1914; L. Kayser, *Zeit. anorg. Chem.*, 138, 43, 1924. A. Leclerc (*Compt. rend.*, 137, 50, 1904) adds to an aqueous solution of the potassium bisulphate fusion enough formic acid to make the solution 5 per cent. acid. On standing two days at 100° all the titanic acid and silica are said to be precipitated.

[4] F. A. Gooch, *Proc. Amer. Acad. Science*, (2), 12, 435, 1885; *Amer. Chem. Journ.*, 7, 283, 1885; *Chem. News*, 52, 55, 68, 1885; T. M. Chatard, *ib.*, 63, 269, 1891; *Amer. Chem.*

the insolubility of titanium hydroxide in solutions containing more than 5 per cent. of acetic acid by volume. The reaction is so delicate that Gooch obtained a distinct opalescence when 0·0005 grm. of titanic oxide was present in 500 c.c. of liquid containing in solution 10 grms. of alum, 15 grms. of sodium acetate and 7 per cent. of acetic acid by volume. The process gives excellent separations of aluminium and titanium, but it does not work well in the presence of iron. The precipitation of basic ferric acetate will be prevented by the presence of 11 per cent. of acetic acid, yet "in the presence of a solution of ferric acetate, titanium shows a very marked tendency to remain dissolved." Thus, 400 c.c. of a solution of 10 grms. of sodium acetate, 17 per cent. of acetic acid and the equivalent of 0·2 grm. of ferric oxide retained 0·06 grm. of titanium oxide in solution.[1] It is advisable to separate the iron as sulphide [2] from the mixture containing aluminium, iron and titanium sulphates. The gravimetric determination involves four operations:—

1. *Separation of Iron from Titanium and Aluminium.*[3]—The iron is best precipitated as ferrous sulphide from the feebly ammoniacal solution containing sufficient tartaric acid to keep the aluminium and titanium in solution. An amount of tartaric acid equal to three times the weight of the oxides to be held in solution is sufficient unless ammonium salts be present in great excess. Hence add, say, 0·7 grm. of tartaric acid to the solution; [4] reduce the iron to ferrous sulphide by means of hydrogen sulphide.[5] Add ammonia until the solution has cleared and the ammonia is in slight excess. Again pass hydrogen sulphide through the solution.[6] The clear supernatant liquid should not be tinted green,[7] though it may be slightly yellow. Filter the solution and wash the precipitate as quickly as possible with water containing ammonium sulphide in solution.[8] The precipitated iron may be dissolved in hydrochloric acid, boiled to expel hydrogen sulphide, oxidised with hydrogen peroxide, precipitated with ammonia, ignited and weighed as Fe_2O_3.

Journ., **13**, 106, 1891; B. Neumann, *Stahl Eisen*, **30**, 457, 1910; H. L. Vogt, *Zeit. prakt. Geol.*, **8**, 379, 1900; W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **700**, 162, 1919; P. T. Austen and F. A. Wilber, *Amer. Chem. Journ.*, **5**, 389, 1883; *Chem. News*, **48**, 113, 1883; G. Werther, *Journ. prakt. Chem.*, (1), **91**, 321, 1864; C. Baskerville, *Journ. Amer. Chem. Soc.*, **16**, 427, 1894; J. W. Bain, *ib.*, **25**, 1073, 1903; H. Wdowiszewski, *Eng. Min. Journ.*, **85**, 1200, 1908; W. M. Thornton, *Eng. Min. Journ.*, **94**, 353, 1912; E. A. Schneider, *Zeit. anorg. Chem.*, **8**, 81, 1895. For the separation of titanium from aluminium by guanidine carbonate, see A. Jílek and J. Kota, *Coll. Czech. Chem. Comm.*, **4**, 412, 1932; by 8-hydroxyquinoline, H. Wabnitz, *Sprechsaal*, **65**, 594, 1932. For the separation of titanium phosphate from aluminium and iron, see E. J. Ericson, *Iron Age*, **72**, 4, 1903; G. S. Jamieson and R. Wrenshall, *Journ. Ind. Eng. Chem.*, **6**, 203, 1914; J. J. Morgan, *Chem. News*, **75**, 134, 1897. C. V. Potapenko (*Keramika i Steklo*, **6**, 29, 1930) describes a method for the determination of titanium and iron in silicates whereby the melt, obtained by fusion with alkali carbonates, can be dissolved without separation of silica. For the determination of titanium as phosphate, see J. C. Ghosh, *Journ. Indian Chem. Soc.*, **8**, 695, 1931.

[1] G. Streit and B. Franz, *Journ. prakt. Chem.*, (1), **108**, 65, 1869.

[2] F. Reich, *Journ. prakt. Chem.*, (1), **83**, 266, 1861; R. Fresenius, *Zeit. anal. Chem.*, **1**, 69, 1862.

[3] Also chromium—J. J. Berzelius, *Pogg. Ann.*, **4**, 3, 1825. Yu. Yu. Lur'e i Podskaya Lab., **3**, 1127, 1934) hydrolyses titanium and aluminium by thiosulphate, while ... remains in solution in the ferrous state.

[4] The tartaric acid must be free from alumina.

[5] A. Cathrein (*Zeit. Kryst.*, **6**, 244, 1882; **7**, 250, 1883) recommends a repetition of the process to recover traces of titanium precipitated with the iron.

[6] Some platinum sulphide may separate. If so, filter and wash. The platinum crucible is slightly attacked during the bisulphate fusion.

[7] Showing that "ferrous" iron is still in solution.

[8] Keep the funnel covered with a clock-glass to prevent oxidation as much as possible, otherwise soluble ferrous sulphate may be formed. For the solubility of ferrous sulphide in alkali sulphides, see A. Konschegg and H. Malfatti, *Zeit. anal. Chem.*, **45**, 747, 1906.

2. *Decomposition of the Tartaric Acid.*[1]—The filtrate and washings may [2] be concentrated by evaporation, the solution acidified with sulphuric acid and sufficient potassium permanganate added to leave the solution distinctly coloured after all the tartaric acid has been oxidised.[3] Generally, about 2·5 times the weight of the tartaric acid is needed. If a deposit of manganese hydroxide is formed, add sulphurous acid until it is dissolved.

3. *Separation of Titanium from Aluminium.*[4]—The solution may now contain manganese, aluminium and titanium, together with some potassium sulphate. Add ammonia until the precipitate first formed dissolves with difficulty on stirring. If the precipitate does not dissolve, a drop or two of hydrochloric acid may be added. Add 20 grms. of sodium acetate and 7 to 10 c.c. of glacial acetic acid for every 100 c.c. of the solution under treatment (that is, about one-tenth the volume of the solution). Heat the solution to boiling and, after boiling one minute, let it stand a few more minutes to allow the flocculent precipitate of titanium hydroxide to subside. Decant the solution through an open-grained filter-paper and wash the precipitate first with 7 per cent. acetic acid and finally with hot water. Dry the precipitate. Ignite 15 to 20 minutes over a Méker's burner. Cool and weigh as TiO_2.

4. *Purification of the Titanium Oxide.*—The titanium oxide carries down some manganese, alumina, alkali sulphates and vanadic acid. For exact work, therefore, the precipitate must be fused with about 10 times its weight of sodium carbonate [5] for about an hour over a blast. A residue of sodium titanate,[6] insoluble in water, remains; sodium phosphate, vanadate and aluminate pass into solution. Filter and wash with water, containing a little sodium carbonate. Dry. Transfer the residue from the filter-paper to a watch-glass. Ignite the filter-paper in the crucible and add the powder in the watch-glass to the ash. Fuse the contents with a little sodium carbonate. Cool. Dissolve in 150 c.c. of water containing 10 c.c. of sulphuric acid (sp. gr. 1·84). Nearly neutralise with ammonia as before and treat the solution with 5 grms. of sodium acetate and one-tenth its volume of glacial acetic acid. Boil one minute, filter and wash as before (*v. supra*). The fusions, precipitations and ignitions should be repeated until the "titanium oxide" obtained is white in colour and constant in weight. Usually the two precipitations indicated above suffice. The purification of the precipitate does not take so long, because the precipitated titanium hydroxide is flocculent and filters easily. In illustration, the following results represent the weights obtained with a titaniferous bauxite:—

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[1] Enough sulphuric acid should be present to leave an excess after all the permanganate subsequently added has formed manganese sulphate. M. Dittrich and R. Pohl (*Zeit. anorg. Chem.*, 43, 236, 1905) prefer oxidising the tartaric acid by evaporating to dryness, and digesting the residue with dilute sulphuric acid and potassium persulphate; W. M. Thornton, jun., (*Amer. J. Science*, (4), 34, 214, 1912; W. R. Schoeller, *Analyst*, 56, 306, 1931) uses a mixture of sulphuric and nitric acids. See page 315. According to W. M. Thornton (*ib.*, (4), 37, 173, 407, 1914), there is no need to oxidise the tartaric acid. After the precipitation of the iron, the hydrogen sulphide is boiled off and 25 c.c. of dilute (1 : 1) sulphuric acid added to every 100 c.c. of the solution. Then sufficient aqua ammonia is added to leave about 2·5 c.c. of the (1 : 1) acid per 100 c.c. of solution, followed by a slight excess of a cold aqueous 6 per cent. solution of cupferron in the cold. Titanium (also zirconium) is precipitated. The titanium precipitate is treated as indicated on p. 504.

[2] A. Fleischer, *Ber.*, 5, 350, 1872; J. Hetper, *Bull. Acad. Science Cracow*, 601, 1910; L. Lindet, *Chem. News*, 76, 212, 1897.

[3] To carbonic and formic acids.

[4] For alternative methods, see L. Moser and E. Irányi, *Monats.*, 43, 673, 679, 1923.

[5] A pink or green coloration is due to manganese.

[6] Iron oxide, if present, will also remain insoluble.

	1st	2nd	3rd	4th	precipitation
	0·0752	0·0699	0·0694	0·0696	grm. TiO_2 obtained.

If zirconium be present, the titanium does not precipitate satisfactorily by this method, since, as Gooch has pointed out, the zirconium oxide acts in a similar manner to the ferric oxide mentioned above. Hillebrand [1] showed that zirconium in presence of titanium prevents the precipitation of the latter, thus: 0·2 per cent. of zirconia in a solution prevented the precipitation of 0·3 per cent. of TiO_2. Hence, Hillebrand recommends the removal of the zirconium as phosphate by the method indicated on page 554 before the titanium is determined.[2]

§ 92. Blair's Modification of Gooch's Gravimetric Process.

If the amount of titanium is large, time can sometimes be saved by determining the amount of titanium in the original sample by Blair's process.[3]

Separation of Iron, etc.—Fuse, say, 1 grm. of the sample with 6–8 times its weight of sodium carbonate and a gram of sodium nitrite. Digest the cold mass with water. Filter off the insoluble residue which contains ferric oxide, sodium titanate, etc.[4] Dry and ignite the residue to burn off the filter-paper.

Solution of Titanium Oxide.—Fuse the residue with 15-20 times its weight of potassium pyrosulphate. When cold, add 2-3 c.c. of concentrated sulphuric acid and heat again until all is melted. Leave a piece of thick platinum wire in the fused mass. When cold, heat the crucible just to soften the cake in contact with the crucible, and transfer the cake, by means of the piece of platinum wire, to a 600 c.c. beaker. Wash the crucible and lid with 5 per cent. sulphuric acid, and make the washings in the beaker up to 150–200 c.c. with the 5 per cent. sulphuric acid.

Precipitation of Titanic Oxide.—Add 50 c.c. sulphurous acid.[5] Warm the solution, but not hotter than can be held comfortably by the hand. This accelerates the solution of the pyrosulphate cake and the acid prevents the precipitation of the titanium at this temperature. If necessary, filter the solution from any silica which may separate. Add ammonia [6] until the precipitate which forms redissolves with difficulty.[7] Treat the solution with 10 c.c. of sulphurous acid, 20 grms. of sodium acetate dissolved in a little water and with acetic acid (sp. gr. 1·06, that is, about 49 per cent.) at the rate of 1 c.c. per 6 c.c. of solution. Heat the solution to boiling, and boil two or three minutes. Flocculent titanic oxide is precipitated. Digest the solution on a steam bath

[1] W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **700**, 164, 1919.

[2] A. R. Powell and W. R. Schoeller (*Analyst*, **55**, 605, 1930) separate titanium from zirconium (and hafnium) by precipitating it with tannin from a neutralised oxalate solution, half-saturated with ammonium chloride. A double precipitation results in a quantitative separation. For the analysis of rutile, see E. W. Hagemaier, *Met. Chem. Eng.*, **16**, 588, 1917; for the determination of titanium oxide in refractory earths, L. Lemal, *Bull. Soc. chim. Belg.*, **36**, 395, 1927; for titaniferous ores, see J. Waddell, *Analyst*, **44**, 307, 1919.

[3] A. A. Blair, *The Chemical Analysis of Iron*, Philadelphia, 184, 1908; F. J. Pope, *Trans. Amer. Inst. Min. Eng.*, **29**, 372, 1899; J. W. Bain, *Journ. Amer. Chem. Soc.*, **25**, 1073, 1903; J. J. Morgan, *Chem. News*, **75**, 134, 1897; G. B. Waterhouse, *ib.*, **85**, 198, 1902; E. Röer, *Chem. Ztg.*, **33**, 1225, 1909 (ilmenite); K. Borneman and H. Schirmeister, *Met.*, **7**, 71, 1911; O. L. Barnebey and R. M. Isham, *Journ. Amer. Chem. Soc.*, **32**, 927, 1910.

[4] Nearly all the phosphorus and aluminium pass into solution as sodium phosphate and aluminate. The filtrate may be used for the determination of other constituents, *e.g.* chlorine, fluorine and sulphur. See pages 746, 725, 703, etc.

[5] Or 5 c.c. of a saturated solution of ammonium bisulphite.

[6] Or add a slight excess of ammonia, and then a few drops of sulphuric acid until the precipitate redissolves.

[7] If platinum is to be removed, the solution should be now treated with hydrogen sulphide.

for half an hour.[1] Let the precipitate settle. Filter and wash first with hot water containing 5 per cent. of acetic acid and finally with hot water. Dry the precipitate. If the precipitate is dark-coloured, instead of white, the titanic oxide may be contaminated with vanadic acid, etc.,[2] in addition to phosphoric acid, alumina, sulphates, etc. The precipitate is purified as indicated for Gooch's process (page 193).

Beans and Mossman [3] have described a method for the determination of titanium by precipitating it as a double potassium titanium iodate—probably $Ti(IO_3)_4.3KIO_3$—which effects its separation from aluminium, calcium, magnesium, nickel, chromates, phosphates, manganese and zirconium; iron, however, must be previously removed. The titanium is subsequently reprecipitated as hydroxide and ignited to the oxide.

§ 93. The Volumetric Determination of Titanium.

Titanium can be determined volumetrically by reduction to the titanous (trivalent) state. The reduced solution is then re-oxidised by titration with a standard solution of a ferric salt.[4] The method is the converse of Knecht's process for iron (page 182).

Owing to the ease and rapidity with which titanous salts are oxidised, great care must be taken that at no time during the determination shall the reduced solution come into contact with the air. The reduction can be effected and a non-oxidising atmosphere maintained as follows:—A 500 c.c. Erlenmeyer's flask is closed by a rubber bung, perforated with three holes. Through the two outer holes pass leading-in and exit tubes for a current of carbon dioxide, and a short length of wide glass tubing, closed at the upper end by a perforated rubber stopper, is fixed through the central hole.

20 c.c. of a 20 per cent. solution of potassium thiocyanate are placed in the flask and the stem of a Jones' reductor (page 173) is fixed through the rubber stopper closing the wide glass tube. A current of carbon dioxide from a Kipp's apparatus is started and allowed to run at a fairly rapid rate until the air in the flask has been entirely displaced. 100 c.c. of 5 per cent. sulphuric acid are passed through the reductor. An aliquot portion, say 50 c.c., of the titanium solution is pipetted out and diluted with an equal volume of 10 per cent. sulphuric acid. After warming to 30°-40°, the mixture is drawn through the reductor in the course of about 10 minutes, gentle suction being applied, if necessary, to the exit tube on the flask. Before the last few c.c. of titanium solution have entered the flask, the reductor is washed out with 100 c.c. of 5 per cent. sulphuric acid, followed by 100 c.c. of distilled water. Both liquids should have been boiled to expel air immediately before use, and then cooled to room temperature. Special care must be taken that at no time during use is the reductor allowed to run dry, otherwise air will be drawn into the flask.

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[1] If filtered immediately, some titanium may be found in the filtrate.
[2] Iron, if carried down from the solution, will be in the ferrous condition or as basic acetate. The addition of about 1 c.c. of 10 per cent. ammonium bisulphite solution before reprecipitation retains any iron in solution.
[3] H. T. Beans and D. R. Mossman, *Journ. Amer. Chem. Soc.*, **54**, 1905, 1932.
[4] G. Gallo, *Atti R. Accad. Lincei*, (5), **16**, 1, 325, 1907; F. W. Hinrichsen, *Chem. Ztg.*, **31**, 738, 1907; E. Hibbert, *Journ. Soc. Chem. Ind.*, **28**, 189, 1909; P. W. and E. W. Shimer, *Eighth Int. Cong. App. Chem.*, **1**, 445, 1912; B. Neumann and R. K. Murphy, *Zeit. angew. Chem.*, **26**, 613, 1913; G. E. F. Lundell and H. B. Knowles, *Journ. Amer. Chem. Soc.*, **45**, 2620, 1923; T. R. Ball and C. M. Smith, *ib.*, **36**, 1838, 1914; K. A. Sukhenko, *Zavodskaya Lab.*, **3**, 499, 1934; H. B. Hope, R. F. Moran and A. O. Ploetz, *Ind. Eng. Chem. Anal. Ed.*, **8**, 48, 1936; G. Röhl, *Chem. Ztg.*, **40**, 105, 1916.

After reduction, the reductor is removed and replaced by the jet of a burette, containing a solution of ferric alum of accurately known iron content.[1]   The titanous solution is now titrated with the standard iron solution until one drop of the latter develops the red colour of ferric thiocyanate.   The current of carbon dioxide, which is maintained throughout the whole of the determination, keeps the solution under titration adequately stirred.

Some little practice is needed to obtain consistent results as, unless care is taken to ensure complete reduction and to preclude subsequent re-oxidation, low values will be reported.[2]

EXAMPLE.—50 c.c. portions of a titanium solution were oxidised by 21·65, 21·60, 21·65 c.c. of a solution of ferric alum containing 0·001589 grm. of iron per c.c.   From the equation

$$Ti_2(SO_4)_3 + Fe_2(SO_4)_3 = 2Ti(SO_4)_2 + 2FeSO_4$$

it follows that 55·84 grms. of iron are equivalent to 47·90 grms. of titanium or 79·90 grms. of titanium dioxide.   Hence each c.c. of the iron solution is equivalent to 0·002274 grm. TiO_2.   Consequently the titanium solution contains $0·002274 \times 21·63 \times 2 = 0·098$ per cent. TiO_2.

§ 94. The Computation of the Results for " Alumina."

The analytical results may now be treated as follows:—

Crucible and ammonia precipitate	20·7003 grms.
Crucible alone	20·4520 ,,
Ammonia precipitate and silica residue . . .	0·2483 grm.
Ash	0·0003 ,,
Alumina, ferric oxide, titanic oxide, etc. . . .	0·2480 grm.
Ferric oxide (p. 185)	0·0156 ,,
Titanic oxide (p. 189)	0·0120 ,,
Phosphoric oxide (p. 672)	0·0000 ,,
Manganese oxide (p. 406)	0·0000 ,,
Extra silica (p. 167)	0·0009 ,,
Sum	0·0285 grm.
Alumina, ferric oxide, etc.	0·2480 ,,
Sum of ferric oxide, etc.	0·0285 ,,
Alumina	0·2195 grm.

The eight alumina determinations in the clay mentioned above thus furnished:

0·2184; 0·2188; 0·2191; 0·2193; 0·2187; 0·2199; 0·2185; 0·2195

grm. Al_2O_3.   The arithmetical mean is 21·90 per cent., and the deviations range between the limits ± 0·10.   If the complete analysis proves faulty when submitted to the test mentioned on page 242, it will generally be found that the fault lies with the alumina determination.

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[1] The air in the dead space of the jet must be replaced by solution *before* the burette is fixed in position.

[2] For the determination of iron and titanium in admixture, see E. Knecht and E. Hibbert, *New Reduction Methods in Volumetric Analysis*, London, 13, 1918; N. Kano, *Journ. Chem. Soc. Japan*, **44**, 47, 1923.

In addition to the disturbing effects of phosphates and fluorides (discussed elsewhere) on the ammonia precipitate, the presence of borates and of oxalates may lead to the precipitation of the barium, strontium, calcium and magnesium salts by ammonia; while the presence of citric and tartaric acids and sugars hinders or prevents the precipitation of iron, aluminium and chromium.[1]

[1] L. J. Cartman and H. Dabin, *Journ. Amer. Chem. Soc.*, 34, 1493, 1912.

CHAPTER XVI.

THE DETERMINATION OF CALCIUM AND MAGNESIUM.

§ 95. The Properties of Calcium Oxalate.

CALCIUM is precipitated from alkaline solutions as hydrated calcium oxalate—$CaC_2O_4 . H_2O$. The precipitate is so difficult to prepare in a form suitable for weighing that it is generally converted by calcination into calcium oxide—CaO. The calcium oxalate obtained by the first precipitation is contaminated to such an extent with sodium and magnesium salts that a second precipitation is advisable. If more magnesium than lime be present, the second precipitation is imperative; if not, one precipitation may be sufficiently exact for the purpose. In illustration, Fresenius [1] gives the following results:—

	Calcium oxide.		Magnesium oxide.	
	Exp. 1.	Exp. 2.	Exp. 1.	Exp. 2.
One precipitation . .	0·2059	0·2063	0·4912	0·4904
Two precipitations .	0·2051	0·2049	0·4927	0·4928

Hence, with one precipitation the lime was 0·0011 grm. (mean) too high, and the magnesia 0·0020 grm. (mean) too low.

Calcium oxalate is precipitated from feebly ammoniacal solutions, and also from solutions acidified with acetic acid,[2] oxalic acid, salicylic acid, or citric acid, by means of ammonium oxalate.[3] Ammonium chloride or sulphate,[4] or an excess of ammonium oxalate,[5] do not interfere very much, but in presence of ammonium salts the precipitate is said to be more difficult to filter. If, however, the pre-

[1] R. Fresenius, *Zeit. anal. Chem.*, 7, 310, 1868; W. Gibbs, *Amer. J. Science*, (2), 44, 213, 1867.

[2] *Chem. News*, 90, 248, 1904; W. Herz and G. Muhs, *Ber.*, 36, 3715, 1903; A. H. Erdenbrecher, *Mikrokosmos*, 16, 201, 1923; L. W. Winkler, *Zeit. angew. Chem.*, 31, 187, 203, 1918.

[3] *Chem. News*, 90, 248, 1904; F. Utz, *Oester. Chem. Ztg.*, 7, 510, 1904.

[4] For the solubility of calcium oxalate in ammonium sulphate solutions, see R. Fresenius, *Zeit. anal. Chem.*, 30, 594, 1891; and in sodium chloride solutions, see A. Gérard, *Ann. Chim. anal.*, 6, 59, 1901. For the solubility in 0·3 to 10 per cent. solutions of ammonium, sodium and magnesium chlorides, ammonium and magnesium sulphates and ammonium nitrate, see K. L. Maljarov and A. J. Gluschakov, *Zeit. anal. Chem.*, 93, 265, 1933. Compare K. Scheringa, *Chem. Weekb.*, 30, 598, 1933.

[5] Zinc, barium and lead, and also cobalt and nickel, if appreciable amounts be present, should be removed before adding the ammonium oxalate. Small quantities of nickel do not interfere when two precipitations are made. Uranium and arsenic do not interfere with the result. Manganese, copper, aluminium, molybdenum and phosphoric acid, if present, will contaminate the precipitate more or less. Chromic acid does not interfere unless it has been reduced to chromic oxide by standing some time—*Chem. News*, 90, 248, 1904.

cipitation be made in hot solutions, or in a solution acidified with acetic acid, the precipitate will be crystalline or granular, and filter easily.

Solubility.—The solubility of calcium oxalate in cold water is, for analytical purposes, negligibly small, but in hot water the solubility becomes appreciable,[1] particularly if the precipitate be subjected to a prolonged washing.   The graph, fig. 71, shows the effect of temperature on the solubility of this salt in water. 100 c.c. of water at 95° will dissolve 0·0015 grm. of calcium oxalate, and at 18° 0·0007 grm.   When first precipitated, calcium oxalate is more soluble than after standing some time, presumably owing to the fact that the fine particles grow into larger grains.[2]

Influence of Magnesium.—A small proportion of magnesium salt accompanies the calcium oxalate precipitate even when a very large amount of ammonium chloride is present, and this particularly when the amount of magnesium is relatively large, or the amount of calcium oxalate relatively small.[3]   On the other hand, a certain amount of calcium escapes precipitation.   Thus, if care be not taken in "separating calcium and magnesium, the result can only represent the truth by a fortuitous balancing of errors, the magnesium precipitated with the calcium compensating the calcium retained in the solution. When the calcium is reprecipitated two or three times, the result must be sensibly low."[4]   This difficulty arises from the fact that calcium oxalate is soluble in magnesium chloride solutions, while magnesium oxalate is but slightly soluble in water.   Hence, sufficient ammonium oxalate must be added to transform all the magnesium chloride into oxalate, and the solution must be so dilute that the magnesium oxalate remains in solution.[5]   Free ammonia
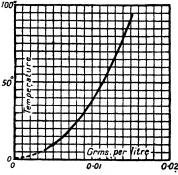
FIG. 71.—Solubility of Calcium Oxalate in Water.

[1] A. F. Holleman, *Zeit. phys. Chem.*, 12, 125, 1893; F. Kohlrausch and F. Rose, *ib.*, 12, 234, 1893; T. W. Richards, C. F. M'Caffrey, and H. Bisbe, *Proc. Amer. Acad.*, 36, 375, 1901; *Zeit. anorg. Chem.*, 28, 71, 1901; H. Bassett, *Journ. Chem. Soc.*, 1273, 1934.

[2] W. H. Wollaston, *Phil. Trans.* 103, 51, 1813; W. Ostwald, *Zeit. phys. Chem.*, 34, 495, 1900; G. Hulett, *ib.*, 37, 385, 1901; 47, 357. 1904.   For the properties of calcium and magnesium salts in reference to the quantitative separation of calcium and magnesium, see C. Blomberg, *Chem. Weekb.*, 11, 1002, 1914; W. Scholvien, *Ueber die Beziehungen zwischen der Wasserlöslichkeit von Oxalaten der alkalischen und seltenen Erden zu ihrer Löslichkeit in sehr verdünnten Sauren sowie über den Einfluss der Korngrösse*, Berlin, 1913; W. Pagireff, *Journ. Russ. Phys. Chem. Soc.*, 34, 195, 1902; O. Brunck, *Zeit. anal. Chem.*, 94, 81, 1933.

[3] For the separation of small quantities of calcium from large amounts of magnesium, see L. Dede, *Chem. Ztg.*, 36, 414, 1912; F. Halla, *ib.*, 38, 100, 1914; R. Heilingötter, *ib.*, 49, 241, 1925; 56, 582, 1932; H. Bach, *ib.*, 49, 514, 1925; G. Luff, *Zeit. anal. Chem.*, 65, 439, 1925.

[4] T. Scheerer, *Journ. prakt. Chem.*, (1), 76, 424, 1859; G. C. Wittstein, *Zeit. anal. Chem.*, 2, 318, 1863; E. Sonstadt, *Chem. News*, 11, 97, 1865; 29, 209, 1874; E. Divers, *ib.*, 11, 144, 1865; M. Longchamp, *Ann. Chim. Phys.*, (1), 12, 255, 1819; E. Lenssen and A. Souchay, *Liebig's Ann.*, 99, 31, 1856; 100, 308, 1856; T. Scheerer, *ib.*, 110, 236, 1859; H. Oeffinger, *Schweiz. Woch. Pharm.*, 6, 265, 1868; F. Hundeshagen, *Zeit. öffent. Chem.*, 15, 85, 1909.

[5] H. Hager, *Pharm. Centr.*, (2), 6, 226, 1865; 10, 241, 1869; W. T. Hall (*Journ. Amer. Chem. Soc.*, 50, 2630, 1928) says that while an excess of ammonium oxalate is necessary, too large an excess makes the subsequent precipitation of magnesium as phosphate incomplete unless the ammonium salts are removed by ignition.   On the other hand, O. Röer (*Tids. Kjemi og Bergwesen*, 9, 27, 1929) limits the quantity of oxalate to that necessary for the complete precipitation of the calcium.   Compare S. Popoff, L. Waldbauer and D. C. McCann, *Ind. Eng. Chem. Anal. Ed.*, 4, 43, 1932.

and warm solutions favour, and the presence of ammonium chloride retards, the precipitation of magnesium oxalate along with the calcium oxalate.[1] Hence, as recommended by Scheerer in 1859, two or three precipitations in the presence of a large excess of ammonium chloride are needed to get rid of the magnesium. Fischer [2] gives the solubility of magnesium oxalate at 18° as only 0·3009 grm. per 1000 c.c., but says that since it forms stable supersaturated solutions, calcium oxalate can be quantitatively separated from it. With an n-fold supersaturation of magnesium oxalate in undisturbed solution and in the presence of ammonium chloride only, perceptible precipitation of magnesium oxalate occurs at time t (hours):—

n	60	50	40	30	25	20	10	4
t	0·5	1	2	3	4	18	40	> 10 weeks

The time is decreased by scratching or warming and by other electrolytes, but increased by certain dyes and gels. Since calcium oxalate is only slowly precipitated, slowly heating to 70°–90° is recommended and, for exact work, the supersaturation of the magnesium oxalate should not be more than fourfold. Hermann [3] likewise attributes the erratic co-precipitation of magnesium with calcium to the influence of supersaturation, the time required for the deposition of magnesium oxalate being lessened by the presence of the calcium salt, by an increase in concentration or a rise in temperature, but increased by ammonium chloride. Many prefer to precipitate the "lime" as calcium sulphate by adding sodium sulphate and an excess of 90 per cent. alcohol, in which calcium sulphate is almost insoluble, while magnesium sulphate is fairly soluble in the same menstruum (see page 589).

Action of Heat.—Calcium oxalate, dried at 100°, has the composition $CaC_2O_4 . H_2O$.[4] At 200° it loses water, forming CaC_2O_4; and at 500° it begins to decompose into calcium carbonate, with the separation of carbon. At the same time the carbon imparts a greyish colour to the mass. At a still higher temperature the carbon burns off, and the carbonate decomposes completely into calcium oxide—CaO—which remains as a white hygroscopic powder.

§ 96. The Gravimetric Determination of Calcium.

If manganese has been determined by the sulphide process (see page 395), the filtrate is boiled for an hour, and filtered from the precipitated sulphur;[5] if manganese is not to be separated, the filtrate from the aluminium and ferric hydroxides is diluted to about 300 c.c. The solution already contains considerable amounts of ammonium chloride; it should contain about 10 grms. per 100 c.c. of the solution per 0·0015 grm. of magnesia.

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[1] W. Pagireff, *Journ. Russ. Phys. Chem. Soc.*, 34, 195, 1902. E. Murmann (*Zeit. anal. Chem.*, 49, 688, 1910) says that "a good separation from magnesium is only possible by adding to the solution of the salts in 90 per cent. alcohol just sufficient sulphuric acid to form calcium sulphate, and washing with 90 per cent. alcohol." "The error is then within 0·15 per cent. of the true value; while the error in the oxalate method is from 0·5 to 2·0 per cent." A. Chizynski, *ib.*, 4, 348, 1865; V. Rodt and E. Kindscher, *Chem. Ztg.*, 48, 953, 964, 1924.

[2] W. M. Fischer, *Zeit. anorg. allgem. Chem.*, 153, 62, 1926; *cf.* M. Lemarchands, *Compt. rend.*, 180, 745, 1925.

[3] Z. Hermann, *Zeit. anorg. allgem. Chem.*, 182, 395, 1929; *ib.*, 184, 289, 1929.

[4] A. Souchay and E. Lenssen, *Liebig's Ann.*, 100, 322, 1856; S. Goy, *Chem. Ztg.*, 37, 1337, 1913; F. Halla, *ib.*, 38, 100, 1914.

[5] Note the possible formation of sulphuric acid, and precipitation of, say, barium as sulphate—C. de la Harpe, *Bull. Soc. Ind. Mulhouse*, 245, 1885.

First Precipitation.[1]—The solution is boiled for a few minutes with 1 to 3 grms. of ammonium oxalate[2] and then a slight excess of concentrated ammonia is added.   After stirring well, the beaker is covered with a clock-glass and stood in a warm place for two hours.   After cooling to room temperature,[3] the precipitate is filtered off and washed two or three times with a cold 1 per cent. solution of ammonium oxalate, the filtrate being reserved for the determination of magnesia.

Second Precipitation.—The precipitate is contaminated with sodium and magnesium salts.[4]   Hence a hole is poked through the apex of the filter-paper and the precipitate is washed into the beaker from which it has just been filtered. The paper is moistened with a few c.c. of nitric acid to dissolve any traces of precipitate and then it is washed with hot distilled water until free from chloride, the washings being collected in the same beaker as before.   The liquid is boiled, more nitric acid being added, if necessary, to complete the solution of the calcium oxalate.   Add a little more ammonium oxalate and make ammoniacal. Boil, stand in a warm place for another two hours, cool, filter [5] and wash with ammonium oxalate solution until free from chlorides.   Care must be taken to remove every trace of the precipitate from the sides of the beaker with a "policeman," since it adheres very tenaciously and is sometimes difficult to see when wet.

The Ignition of the Precipitate.—Place the moist filter-paper in an ignited and weighed crucible.   Heat gently until the paper is charred—fig. 74—then incinerate the precipitate with the crucible inclined at an angle of, say, 45°, so as to burn the carbon mixed with the oxalate.   Blast about 15 minutes, or heat over a Méker's burner or in a Davies crucible furnace, thereby raising the temperature above that possible with an unprotected flame.   Cool the crucible in a desiccator,[6] and weigh as quickly as possible to avoid the absorption of carbon dioxide and moisture [7] from the atmosphere.   The crucible and pre-

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[1] E. Murmann, *Monats.* 32, 105, 1911; *Oester. Chem. Ztg.*, 12, 305, 1909; *Zeit anal. Chem.*, 49, 688, 1910.

[2] At least four times as much ammonium oxalate is required beyond that needed to form calcium oxalate with the lime, and magnesium oxalate with the magnesia.   Note that commercial ammonium oxalate sometimes contains calcium salts.

[3] Where the greatest accuracy is not essential, time can be saved by filtering off the hot solution and washing the precipitate with hot distilled water, both here and in the second precipitation.

[4] T. Scheerer, *Journ. prakt. Chem.*, (1) 79, 424, 1859; A. Cossa, *Zeit. anal. Chem.*, 8, 141, 1869; T. W. Richards, *Zeit. anorg. Chem.*, 23, 383, 1900; W. C. Blasdale, *Journ. Amer. Chem. Soc.*, 31, 917, 1909; C. Stolberg, *Zeit. angew. Chem.*, 17, 741, 769, 1904; R. Hefelmann, *Zeit. öffent. Chem.*, 3, 193, 1897; N. Knight, *Chem. News*, 89, 146, 1904; C. Liesse, *Bull. Assoc. Chim. Sucr. Dist.*, 28, 559, 1910; F. H. McCrudden, *Journ. Biol. Chem.*, 10, 187, 1911.

[5] A Gooch crucible may be used.

[6] Containing concentrated sulphuric acid.   According to O. Brunck (*Zeit. angew. Chem.*, 17, 953, 1904), the oxide should be dried over sulphuric acid, because the carbon dioxide of the air may lead to the evolution of chlorine by calcium chloride.   It might be questioned whether this action could affect the result appreciably.   A. Franke and R. Dworzak (*Zeit. anal. Chem.*, 72, 129, 1927) recommend drying over phosphorus pentoxide, while H. S. Booth and L. McIntyre (*Ind. Eng. Chem. Anal. Ed.*, 8, 148, 1936) advocate porous barium oxide, since it maintains a carbon dioxide-free atmosphere in the desiccator.   R. Cernatesco and E. Văscautan (*Ann. Sci. Univ. Jassy*, 14, 305, 1928) ignite in a current of oxygen to reduce the time of obtaining constant weight.

[7] To illustrate the hygroscopicity of the powder, R. Fresenius (*Quantitative Chemical Analysis*, London, 2, 633, 1900) states that 0·5599 grm. of calcium oxide weighed 0·5605 grm. after standing 2 minutes on the pan of the balance; 0·5609 grm. after standing 6 minutes; and 0·5625 grm. after standing 17 minutes.   H. Bassett (*Journ. Chem. Soc.*, 1273, 1934) corrects for the absorbed moisture by deducting 0·5 mgrm. from the weight of small precipitates and 0·7 mgrm. from the weight of large precipitates (up to 0·1 grm.).

cipitate are again ignited for 5 to 10 minutes, cooled and re-weighed, to make sure that the conversion of the oxalate to oxide was complete.[1]

Other Methods of Weighing the Precipitate.—Instead of weighing the calcium in the form of oxide,[2] some prefer to convert the oxalate into carbonate,[3] or sulphate, or tungstate,[4] or weigh the oxalate as such.[5] The objection is made that in converting the oxalate into oxide the crucible loses weight during the 15 minutes' blasting,[6] and the oxide is difficult to weigh on account of its hygroscopicity. If small quantities are in question, conversion of the oxalate into sulphate has the advantage of giving a larger weight of residue.

Conversion of Calcium Oxalate to Calcium Sulphate.—First ignite the oxalate at a comparatively low temperature, sufficient to burn the paper and convert most of the oxalate into oxide. Add one or two c.c. of water, gradually, drop by drop, to avoid spurting. This treatment will transform the calcium oxide into hydroxide. Add a slight excess of dilute sulphuric acid; drive off the excess with a small flame, taking care to avoid loss by spurting, which will occur if the crucible be heated too rapidly.[7] Finally ignite the crucible at a dull red heat; weigh the resulting calcium sulphate—$CaSO_4$—and multiply the weight by 0·4119 in order to get the equivalent amount of CaO.

Souchay [8] examined the results obtained by weighing the lime as oxalate, as carbonate, as sulphate, and as caustic lime, with the following results:—

	Oxalate.	Carbonate.	Sulphate.	Oxide.
CaO	38·12	38·09	38·06	38·12 per cent.

Hence it follows that, with care, all the methods furnish satisfactory results. In cases like this, where different methods give equally reliable results, the choice of any particular process is determined by convenience, risk of error and time.

Errors.—The following numbers represent the results of eight independent determinations by the "oxalate to oxide" process on one sample of clay:—

0·0137; 0·0141; 0·0147; 0·0142; 0·0152; 0·0152; 0·0141; 0·0142

with a mean value of 0·0144 grm. CaO corresponding with 1·44 per cent. CaO. The deviations from the mean are ±0·08.

[1] If the clay contains strontia, this will be precipitated with the lime. To determine the strontia, convert the precipitates to nitrates and digest the mixture with a mixture of absolute alcohol and ether (page 578). The calcium nitrate is washed away, and the insoluble strontium nitrate is ignited and weighed as SrO. The CaO is obtained by subtraction from the weight of mixed CaO + SrO. L. Szebellédy, *Magyar Chem. Fol.*, **35**, 59, 1929; *Chem. Zentr.*, (2), 274, 1930.

[2] A. Fritzsche, *Zeit. anal. Chem.*, **3**, 177, 1864.

[3] H. W. Foote and W. M. Bradley, *Journ. Amer. Chem. Soc.*, **48**, 676, 1926; H. H. Willard and A. W. Boldyreff, *ib.*, **52**, 1888, 1930.

[4] A. Saint-Sernin, *Compt. rend.*, **156**, 1019, 1913.

[5] S. Goy, *Chem. Ztg.*, **37**, 1337, 1913; H. Sibelius, *Suomen Kemistilehti*, **8A**, 25, 1935.

[6] O. Brunck, *Zeit. anal. Chem.*, **45**, 77, 1906.

[7] The use of the ring burner reduces to a minimum the risk of loss by spurting. E. Kettler, *Zeit. angew. Chem.*, **17**, 685, 1904; O. Brunck, *ib.*, **17**, 953, 1904; E. Murmann, *Zeit. anal. Chem.*, **49**, 688, 1910; A. N. Clark, *Journ. Amer. Chem. Soc.*, **26**, 110, 1904. F. B. Guthrie and C. R. Barker (*Journ. Roy. Soc. N.S.W.*, **36**, 132, 1902) ignite the oxalate with ammonium nitrate equal to the bulk of the lime in the crucible; and W. H. Hess (*Journ. Amer. Chem. Soc.*, **22**, 477, 1900) then adds twice as much ammonium sulphate, ignites at a dull red heat and weighs as calcium sulphate. A. Schrötter (*Die Chemie*, Wien, 2, 1849) uses ammonium sulphate alone. For the decomposition of calcium and magnesium sulphates by heat, see A. Mitscherlich, *Journ. prakt. Chem.*, (1), **83**, 485, 1861; J. Boussingault, *Compt. rend.*, **64**, 1159, 1867; W. Schütz, *Metallurgie*, 8, 228, 1910.

[8] A. Souchay, *Zeit. anal. Chem.*, **10**, 323, 1871; R. Fresenius, *ib.*, **10**, 326, 1871; G. E. Ewe, *Chem. News*, **121**, 53, 1920; A. Franke and R. Dworzak, *Zeit. anal. Chem.*, **72**, 129, 1927.

§ 97. The Volumetric Determination of Lime—Kraut's Process.

For routine work with calcareous clays, it is quickest to determine the lime volumetrically.[1] Poke a hole through the apex of the paper carrying the precipitated and washed calcium oxalate; wash the calcium oxalate from the paper by means of a jet of hot water, and then with dilute sulphuric acid (1 : 4) taking care to wash well under the folds of the paper.   Add 10 c.c. of concentrated sulphuric acid and titrate the hot solution (60°-70°) with standard permanganate, as indicated for sodium oxalate (page 176), until the solution is tinged with a permanent pink colour.

The reaction which takes place during the titration is represented by the equation

$$5CaC_2O_4 + 2KMnO_4 + 8H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5CaSO_4 + 8H_2O + 10CO_2$$

This shows that 1 grm. of $KMnO_4$ corresponds with 0·8872 grm. of CaO.

EXAMPLE.—The permanganate solution used in a titration contained 2·4 grms. of $KMnO_4$ per litre, and 20·5 c.c. were used to oxidise the calcium oxalate obtained from one gram of the sample.   Hence 100 grms. of the sample will require 2·05 litres of the permanganate solution or $2·05 \times 2·4$ grms. of permanganate.   Consequently the sample contains $2·05 \times 2·4 \times 0·8872 = 4·36$ per cent. of calcium oxide—CaO.   The method is not recommended when but a few determinations are made, and it is only used when a large number of analyses have to be conducted concurrently.

§ 98. The Properties of Ammonium Magnesium Phosphate.

A precipitate of ammonium magnesium phosphate is obtained in the determination of magnesia by adding a soluble phosphate to the ammoniacal solution containing the magnesium compound.

Composition of the Precipitate.—According to Neubauer,[2] the precipitation is practically complete, even in the presence of comparatively large quantities of ammonium salts, including the oxalate, but the composition of the precipitate is largely determined by the nature of the solution.   The ammonium magnesium phosphate may exist in three different forms, according to the composition of the mother liquid at the time of precipitation:—

1. In neutral or ammoniacal solutions, the precipitate is tetrammonium magnesium diphosphate, $Mg(NH_4)_4(PO_4)_2$. This contains less magnesium

[1] W. Hempel, *Mémoires sur l'emploi de l'acide oxalique dans les dosages à liqueurs titrées,* Lausanne, 1853; K. Kraut, *Henneberg's Landwirthsch.*, (1), **4**, 112, 1856; *Zeit. anal. Chem.*, **26**, 629, 1887; L. T. Bowser, *Journ. Ind. Eng. Chem.*, **3**, 82, 1911; G. P. Baxter and J. C. Zanette, *Amer. Chem. Journ.*, **33**, 500, 1905; H. Walland, *Chem. Ztg.*, **27**, 922, 1903; C. H. Schultze, *ib.*, **29**, 508, 1905; B. Enright, *Journ. Amer. Chem. Soc.*, **26**, 1003, 1904; T. Ulke, *Monit. Scient.*, (4), **14**, 775, 1908; M. Kruger, *Zeit. physiol. Chem.*, **16**, 445, 1892; G. Lunge, *Zeit. angew. Chem.*, **17**, 265, 1904; J. Volhard, *Liebig's Ann.*, **198**, 333, 1879; E. Rupp and A. Bergdolt, *Archiv Pharm.*, **242**, 450, 1904; C. A. Peters, *Zeit. anorg. Chem.*, **29**, 145, 1902; H. M. Davy, *Chem. News*, **29**, 250, 1874; *Compt. rend.*, **78**, 978, 1874; A. Heifer, *Tonind. Ztg.*, **18**, 535, 1894; K. von Radlowski, *ib.*, **18**, 592, 1894; Hornke, *ib.*, **61**, 311, 1937; T. Döring, *Zeit. angew. Chem.*, **26**, 478, 1913; J. Grossfeld, *Chem. Ztg.*, **41**, 842, 1917; H. Bassett, *Journ. Chem. Soc.*, 1273, 1934; L. Velluz and R. Deschaseaux, *Bull. Soc. chim. biol.*, **13**, 797, 1931; *Compt. rend. Soc. biol.*, **104**, 976, 1931; F. L. Hahn and G. Weiler, *Zeit. anal. Chem.*, **70**, 1, 1927; J. Haslam, *Analyst*, **60**, 668, 1935.

[2] H. Neubauer, *Ueber die Zuverlässigkeit der Phosphorsäurebestimmung als Magnesiumpyrophosphat*, Rostock, 1893; *Journ. Amer. Chem. Soc.*, **16**, 289, 1894; W. Heintz, *Zeit. Chem.*, (2), **6**, 479, 1870; O. Popp, *ib.*, (2), **6**, 395, 1870; K. Bube, *Ueber Magnesiumammoniumphosphat*, Weisbaden, 1910; R. Reidenbach, *Ueber die quantitative Bestimmung des Magnesiums als Magnesiumpyrophosphat*, Kusel, 1910; P. Schottländer, *Zeit. anorg. Chem.*, **7**, 343, 1894.

than the normal magnesium ammonium phosphate, $MgNH_4PO_4$. The former compound, on calcination, decomposes, forming magnesium metaphosphate, water and ammonia:

$$Mg(NH_4)_4(PO_4)_2 \rightarrow Mg(PO_3)_2 + 4NH_3 + 2H_2O$$

On further calcination, the metaphosphate decomposes into magnesium pyrophosphate and phosphoric anhydride:

$$2Mg(PO_3)_2 \rightarrow Mg_2P_2O_7 + P_2O_5$$

and some phosphoric anhydride is volatilised.[1]

2. When an excess of magnesium salt is present, and no excess of ammonia, the precipitate has the normal composition—$MgNH_4PO_4$—and the results are correct.

3. If an excess of magnesium salt and an excess of ammonia be present, the precipitate contains more magnesium than the normal phosphate, and the calculated phosphoric acid will be too high.

Nerl has verified the first, and Reidenbach the second observation of Neubauer; but Reidenbach considers that the third observation is not correct. He found the precipitate contained less, not more, magnesium than Neubauer's statement represents.

In any case, it is necessary to precipitate the ammonium magnesium phosphate in a solution containing definite amounts of ammonia, ammonium salts, magnesia and phosphoric acid in order to obtain concordant results.[2] The precipitant should also be added to the *acid* solution, and the ammonia in slight excess added *afterwards*.

Solubility of Ammonium Magnesium Phosphate.—The precipitate is readily soluble in dilute acids, and 100 c.c. of water at 10° dissolve 0·0065 grm. of the salt.[3] It is much less soluble in aqueous ammonia.[4] Thus, according to Stünkel, Wetzke and Wagner, solutions containing p per cent. of ammonia dissolve per litre:—

p	.	.	.	.	.	.	1	2	3	per cent.
MgO	.	.	.	.	.	.	0·00050	0·00023	0·00008	grm.
P_2O_5	.	.	.	.	.	.	0·00088	0·00038	0·00015	,,

The solubility of the ammonium magnesium phosphate in ammonia is also illustrated by graph, fig. 72, which shows that the solubility of normal ammonium magnesium phosphate decreases very rapidly with increasing concentration of ammonia.[5] According to Jörgensen, the solubility in 2·5 per cent. ammonia is approximately 0·00006 grm. of MgO per 100 c.c. This is negligibly

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[1] D. Campbell, *Phil. Mag.*, (4), **24**, 380, 1862. D. Balareff (*Zeit. anorg. Chem.*, **103**, 73, 1918) says that the decomposition is $Mg(NH_4)_4(PO_4)_2 = MgNH_4PO_4 + (NH_4)_3PO_4$. On further heating, magnesium pyrophosphate is formed, the ammonium phosphate decomposes, some phosphorus pentoxide being volatilised, while the remainder reacts with the pyrophosphate to give metaphosphate.

[2] D. Balareff, *Zeit. anorg. Chem.*, **102**, 241, 1918.

[3] K. Bube (*Zeit. anal. Chem.*, **49**, 588, 1910) made some observations on the solubility of this salt. See also P. Wenger, *Étude sur la solubilité des phosphates et des arséniates ammoniaco-magnésiens et du phosphate ammoniaco-manganeux*, Genève, 1911; *Tables annuelles de Constantes*, Paris, **2**, 411, 1911.

[4] G. Jörgensen, *Mem. Acad. Roy. Soc. Danemark*, (7), **2**, 141, 1905; C. Stünkel, T. Wetzke and F. Wagner, *Zeit. anal. Chem.*, **21**, 353, 1882; T. R. Ogilvie, *Chem. News*, **31**, 274, 1875; **32**, 5, 12, 70, 1875; E. W. Parnell, *ib.*, **32**, 222, 1875; **23**, 145, 1871; P. Wenger, *l.c.*

[5] According to A. Bolis (*Chem. Ztg.*, **27**, 1151, 1903), 2 grms. of $MgNH_4PO_4.6H_2O$ in contact with 100 c.c. of a solution of ammonium citrate (400 grms. of citric acid per litre) loses, by solution, an average of 0·457 per cent. in weight at ordinary temperatures, and 0·587 per cent. at 50°.

small.[1] The solubility is increased in solutions of ammonium chloride, so that 0·0013 grm. is dissolved per 100 c.c. in the presence of 2·5 per cent. ammonia containing a gram of ammonium chloride. The effect of ammonium chloride
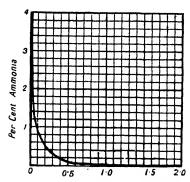
FIG. 72.—Effect of Ammonia on the Solubility of Ammonium Magnesium Phosphate (mgrms. MgO per 100 c.c.).
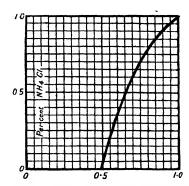
FIG. 73.—Effect of Ammonium Chloride on the Solubility of Ammonium Magnesium Phosphate (mgrms. MgO per 100 c.c.).

on the solubility of the magnesium ammonium phosphate is illustrated by the graph, fig. 73.

When, however, precipitation takes place in the presence of ammonium chloride, curiously enough in view of fig. 73, precipitates with positive, not negative, errors are obtained; otherwise expressed, the results are too high. For example,

NH_4Cl	.	.	0	2·67	5·35	10·70	grms. per litre
$Mg_2P_2O_7$	.	.	0·5567	0·5603	0·5612	0·5619	grm.
Error	.	.	..	+0·0036	+0·0045	+0·0052	,,

The solution from which the magnesium phosphate is first precipitated usually contains not only ammonium chloride and ammonia, but also ammonium oxalate, and considerable amounts of sodium chloride. The effect of ammonium oxalate, like ammonium chloride, is to raise the weight of the precipitate above the normal.[2] Thus,

$(NH_4)_2C_2O_4$	.	.	0	3·55	4·26	4·97	grms per litre.
$Mg_2P_2O_7$	.	.	0·5567	0·5900	0·5864	0·5863	grm.
Error	.	.	..	+0·0333	+0·0297	+0·0296	,,

The presence of sodium chloride in the mother liquid also considerably augments the weight of the resulting precipitate. Thus,

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[1] There is therefore no need to correct for the solvent action of the wash liquids as recommended by C. R. Fresenius, *Anleitung zur quantitative chemischen Analyse*, Braunschweig, 1, 333, 1863; *Liebig's Ann.*, 55, 111, 1845; R. Warington, *Journ. Chem. Soc.*, 18, 27, 1865; W. Kübel, *Zeit. anal. Chem.*, 8, 125, 1869; O. Abesser, W. Jani, M. H. Märcker, *ib.*, 12, 239, 1873; F. A. Gooch, *Amer. Chem. Journ.*, 1, 391, 1879; T. S. Gladding, *Chem. News*, 46, 213, 1882; 47, 71, 1883. Three solutions containing the same amount of magnesia were precipitated in exactly the same way, but the precipitates were respectively washed with a litre of 1, 2 and 3 per cent. ammonia. The corresponding precipitates gave 0·1956, 0·1967, 0·1968 grm. of ammonium magnesium phosphate. Theory required 0·1971 grm. Nothing like a litre of washing liquid is required in practice, so that the errors due to the solubility of the precipitate must be negligibly small.

[2] W. T. Hall (*Journ. Amer. Chem. Soc.*, 50, 2630, 1928; V. T. Chuiko, *Journ. App. Chem. U.S.S.R.*, 10, 364, 1937) claims that an excess of ammonium oxalate makes the precipitation of magnesium incomplete.

NaCl	.	.	0	0·585	5·85	23·4	grms. per litre
$Mg_2P_2O_7$	.	.	0·5567	0·5585	0·5689	0·5770	grm.
Error	.	.	..	+0·0018	+0·0122	+0·0203	,,

The effect with potassium chloride is much greater than with sodium chloride. The practical lesson to be learned from these observations is that *the magnesium ammonium phosphate first precipitated must be dissolved in dilute acid and reprecipitated, otherwise the result will be of little value.*

The precipitate is more soluble in hot solutions. With hot solutions there is also a loss of ammonia. Hence the precipitation should be made in cold solutions, with an excess of the precipitating agent, and in the presence of at least 2·5 per cent. of ammonia. The precipitate made in solutions containing ammonium salts—chloride and oxalate—and sodium chloride is very impure,[1] and it must in consequence be dissolved in dilute acid and reprecipitated as described below.

Action of Heat.—Ammonium magnesium phosphate—$MgNH_4PO_4 . 6H_2O$— loses $5H_2O$ at about 100°, and the remaining H_2O with the ammonia, at a red heat, forming magnesium pyrophosphate.

$$2(MgNH_4PO_4 . 6H_2O) = Mg_2P_2O_7 + 2NH_3 + 13H_2O$$

If the temperature be raised still further, the pyrophosphate becomes incandescent, owing to an intramolecular change—according to Popp,[2] a passage from the crystalline to an amorphous condition. The magnesium pyrophosphate fuses at 1220°. If magnesium pyrophosphate be exposed to a reducing atmosphere at a high temperature, phosphorus and phosphine are said to be volatilised.[3] These vapours attack the platinum crucibles. The pyrophosphate is soluble in dilute nitric and hydrochloric acids, but sparingly soluble in water.

Precipitation of Ammonium Magnesium Phosphate for the Determination of Phosphorus.—An excess of magnesium chloride (magnesia mixture, page 284) reduces the solubility [4] of magnesium ammonium phosphate even more than an excess of the phosphate solution. No phosphoric acid, for example, could be detected in a filtrate which would, without the excess magnesium chloride, have contained the equivalent of 0·0025 grm. P_2O_5. An excess of a soluble phosphate also reduces the solubility of the ammonium magnesium phosphate in a similar manner.

§ 99. The Gravimetric Determination of Magnesia.

The magnesia is determined in the ammoniacal filtrate from the calcium oxalate [5] by the addition of a soluble phosphate; a precipitate of ammonium

[1] H. Neubauer, *Zeit. angew. Chem.*, 9, 435, 1896; *Zeit. anorg. Chem.*, 2, 45, 1892; 4, 251, 1893; R. Woy, *Chem. Ztg.*, 21, 441, 1897; F. A. Gooch and M. Austin, *Zeit. anorg. Chem.*, 20, 121, 1899; F. L. Harn, K. Vieweg and H. Meyer, *Ber.*, 60B, 971, 1927; A. W. Epperson, *Journ. Amer. Chem. Soc.*, 50, 321, 1928; J. I. Hoffmann and G. E. F. Lundell, *Bur. Stand. Journ. Research*, 5, 279, 1930; L. W. Winkler, *Zeit. angew. Chem.*, 31, 211, 1918.

[2] O. Popp, *Zeit. anal. Chem.*, 13, 305, 1874.

[3] H. Struve, *Journ. prakt. Chem.*, (1), 79, 349, 1860; R. Weber, *Pogg. Ann.*, 73, 146, 1848.

[4] W. Heintz, *Zeit. anal. Chem.*, 9, 16, 1870; E. Kessel, *ib.*, 8, 173, 1869; W. Kübel, *ib.*, 8, 125, 1869; R. Weber, *Pogg. Ann.*, 73, 139, 1848. Basic magnesium phosphate is precipitated if the magnesia mixture be in large excess, and magnesium sulphate is used in place of magnesium chloride for compounding the magnesia mixture (page 674).

[5] Clays normally contain so little magnesia that the filtrate from the first precipitation of the lime is alone taken for the determination of the magnesia, but with materials relatively high in magnesia the combined filtrates from each precipitation of the lime must be used after evaporation, if necessary, to convenient bulk.

magnesium phosphate separates. Unfortunately, the composition of the precipitate is considerably modified by the composition of the solution in which the precipitation takes place.[1] The precipitate is therefore redissolved, and reprecipitated under definite conditions whereby a precipitate of the composition $MgNH_4PO_4.6H_2O$ is obtained. This is ignited and weighed as $Mg_2P_2O_7$.

First Precipitation.—Gradually add a solution containing, say, 2 grms. of sodium ammonium phosphate [2] (dissolved in 15 c.c. of water) to the solution under investigation,[3] with constant stirring. While still stirring the solution,[4] gradually add, drop by drop, about one-third its volume of aqueous ammonia; cover the solution with a clock-glass,[5] and let it stand 12 to 24 hours. Stir very thoroughly [6] and then filter. There is no particular need here to clean the precipitate from the bottom and sides of the beaker. Wash the precipitate with

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[1] H. Struve, *Zeit. anal. Chem.*, 36, 289, 1897; 37, 485, 1898; K. K. Järvinen, *ib.*, 43, 279, 1904; 44, 333, 1905; R. Fresenius, H. Neubauer, and E. Luck, *ib.*, 10, 133, 1871; C. Schumann, *ib.*, 11, 382, 1872; H. Schmidt, *ib.*, 45, 512, 1906; H. Neubauer, *Zeit. angew. Chem.*, 9, 435, 1896; F. Raschig, *ib.*, 18, 374, 1905; F. A. Gooch and M. Austin, *Amer. Journ. Science*, (4), 7, 187, 1899; W. Gibbs, *ib.*, (3), 5, 114, 1873; *Chem. News*, 28, 51, 1873; R. W. C. MacIvor, *ib.*, 28, 69, 1873; T. R. Ogilvie, *ib.*, 21, 205, 1870; F. A. Gooch, *Amer. Chem. Journ.*, 1, 391, 1879; A. K. Christomanos, *Zeit. anorg. Chem.*, 41, 305, 1904; T. S. Gladding, *Journ. Amer. Chem. Soc.*, 4, 135, 1882; *Chem. News*, 46, 213, 1882; E. Raffa, *Gazz. Chim. Ital.*, 38, ii, 556, 1908; M. Wunder and C. Schuller, *Ann. Chim. anal.*, 18, 221, 1913; G. Chancel, *Compt. rend.*, 50, 94, 1860; J. C. Hostetter, *Journ. Ind. Eng. Chem.*, 6, 392, 1914; G. H. Brother, *ib.*, 10, 129, 1918; B. Schmitz, *Zeit. anal. Chem.*, 65, 46, 1924.

[2] J. J. Berzelius (*Lehrbuch der Chemie*, Dresden, 2, 650, 1826) used disodium phosphate. C. Mohr prefers sodium ammonium phosphate—microcosmic salt (*Zeit. anal. Chem.*, 12, 36, 1873; W. Gibbs, *l.c.*)—because it precipitates more rapidly and completely. By precipitating more and more dilute solutions of magnesia, he arrived at a point where sodium phosphate no longer gave a precipitate under conditions where sodium ammonium phosphate did. L. Blum (*Zeit. anal. Chem.*, 28, 452, 1889; W. Heintz, *ib.*, 9, 16, 1870; L. Blum *Stahl Eisen*, 34, 487, 1914) prefers disodium phosphate, because the precipitate settles more rapidly and filters more quickly than when sodium ammonium phosphate is the precipitating agent. See also L. A. Congdon and G. Vanderhook, *Chem. News*, 130, 241, 258, 273, 1925.

[3] K. L. Malyarov and V. B. Matskievich (*Zeit. anal. Chem.*, 98, 31, 1934) find that in solutions of sodium and ammonium chlorides and sulphates, ammonium nitrate and ammonium oxalate, the solubility of magnesium ammonium phosphate in all cases increases with the concentration of the salt present. Ammonium nitrate has the smallest solvent effect, and ammonium oxalate the greatest—a 5 per cent. solution of the latter salt dissolving no less than 0·7690 grm. of magnesium ammonium phosphate per litre. In order to get rid of the ammonium salts which have accumulated in the solution during the removal of the alumina and lime, the filtrate is evaporated nearly to dryness in a large dish. Add concentrated nitric acid, evaporate the solution to dryness and heat the residue until all the ammonium salts have volatilised. Dissolve the mass in water, filter off any insoluble matter and treat the solution as described in the text. The insoluble residue may be examined for alumina. This, if present, is precipitated, washed and weighed as "extra alumina." J. Jámbor, *Zeit. anal. Chem.*, 49, 733, 1910; O. Kallauner, *Zement*, 16, 1093, 1927; W. T. Hall, *Journ. Amer. Chem. Soc.*, 50, 2630, 1928. See page 217. Tests indicate that there is little advantage, if any, in removing the ammonium salts when dealing with amounts of magnesia normally present in a clay.

[4] This point requires careful attention. The precipitate will be more contaminated with impurities if quickly made. In illustration, a mean of six experiments in which the solutions were mixed suddenly gave 0·2028 grm. of $Mg_2P_2O_7$; another six experiments with the ammonia gradually mixed with constant stirring gave 0·1972 grm. $Mg_2P_2O_7$. Theory required 0·1971 grm. $Mg_2P_2O_7$. The stirring rod should be kept from the sides and bottom of the beaker. See H. Lasne, *Bull. Soc. chim.*, (3), 17, 823, 1897; *Chem. News*, 76, 270, 1897.

[5] Some keep the beaker under a bell jar resting on a greased ground-glass plate in order to prevent the evaporation of ammonia.

[6] Precipitates which take a long time to separate on standing frequently come down quickly if the solution be vigorously agitated—by, say, bubbling a current of air through the solution, or mechanical agitation—L. Briant, *Chem. News*, 53, 99, 1886; O. Texter, *Journ. Anal. App. Chem.*, 7, 279, 1893; V. Markoonikoff, *Liebig's Ann.*, 289, 254, 1895; H. B. Yardley, *New Remedies*, 9, 333, 1880.

dilute ammonia (1 : 10, that is, about 2·5 per cent.).[1] Reject the filtrate, which should give a precipitate with "magnesia mixture" (page 284). When the washing is completed, the runnings will give no precipitate with silver nitrate in acid (HNO_3) solution. Reject the filtrate and washings.

Second Precipitation.—Redissolve the precipitate in warm dilute nitric acid (1 : 5), and collect the washings in the beaker in which the first precipitation was made. About 50 c.c. of acid are needed. While the acid is running through the funnel, turn the beaker round so that the acid runs all round the sides of the beaker. Add an aqueous solution containing a little sodium ammonium phosphate, and then add ammonia gradually with constant stirring, as in the first precipitation. Stand for 12 hours, again stir very thoroughly before filtering, wash as before; reject the filtrate and washings.

Ignition of the Precipitate.[2]—The precipitate may be collected on a Gooch asbestos[3] crucible prepared in the usual manner. After the crucible has been dried and heated slowly over a Bunsen burner (in a Gooch crucible saucer, page 92), it is heated over the Teclu or Méker burner for about 10 minutes. Cool in a desiccator and weigh. Ignite 4 or 5 minutes, cool and weigh again. Repeat the ignition if necessary, until the weight is constant.[4]

If the precipitate be collected on a 7 cm. filter-paper, the moist paper is placed in the crucible, dried and carbonised very slowly in the (platinum or porcelain) crucible, placed obliquely on a triangle over, say, an Argand burner,[5] fig. 74. The temperature is gradually raised to redness, and there maintained until the precipitate appears white.[6] Finish the ignition over a weak blast.

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[1] G. Surr, *Min. Eng. World*, **41**, 1167, 1914.

[2] K. Brookman (*Zeit. anal. Chem.*, **21**, 551, 1882) dissolves the precipitate in nitric acid, and evaporates the solution to dryness in a weighed dish, ignites, etc. The object is to avoid loss (1) by the sticking of the precipitate to the walls of the beaker; (2) the "crawling" of the finely divided precipitate above the edge of the filter-paper on to the funnel during washing; (3) as "dust" during the transfer of the dry filter-paper to the crucible; and (4) loss as "dust" during the collapse of the ash of the filter-paper during the ignition in the crucible. L. L. de Koninck (*Zeit. angew. Chem.*, **1**, 427, 1888; *Zeit. anal. Chem.*, **29**, 165, 1890; R. Fresenius, *ib.*, **15**, 224, 1876; **16**, 63, 1877) recommends a similar procedure for precipitates liable to reduction from the combustion of the filter-paper, *e.g.* ammonium and potassium chloroplatinates, ammonium magnesium arsenates and phosphates; cadmium and zinc carbonates. For weighing the precipitate as ammonium magnesium phosphate, $Mg(NH_4)PO_4 . 6H_2O$, see W. Jones, *Journ. Biol. Chem.*, **25**, 87, 1916.

[3] H. N. Warren (*Chem. News*, **61**, 63, 1890) recommends a plug of gun-cotton (pyroxylin) in place of asbestos. This burns away on ignition. See J. L. Jodidi and E. H. Kellogg, *Journ. Franklin Inst.*, **181**, 217, 1916, for filtration with paper pulp.

[4] M. Wunder and C. Schuller, *Ann. Chim. anal.*, **18**, 221, 1913; S. S. Miholić, *Journ. Chem. Soc.*, 200, 1930.

[5] It is not generally advisable to rest the triangle on the chimney of the Argand burner, because the draught may be choked. The crucible is best supported on a triangle as shown in the diagram. If the precipitate be large, it should be dried and separated from the filter-paper, so that the filter-paper can be ignited alone. If a platinum crucible be used for the ignition of the phosphate, and reducing agents (like carbon from the filter-paper, reducing gases, hydrogen liberated from the decomposition of ammonia at high temperatures, etc.) be present, phosphides may be formed. These attack the platinum (W. C. Heraeus, *Zeit. angew. Chem.*, **15**, 917, 1902; *Chem. News*, **97**, 102, 1903; W. P. Headden, *Proc. Colorado Scientific Soc.*, **8**, 45, 1905). Under ordinary conditions, however, there is little danger of this occurrence during the ignition of the magnesium phosphates if the temperature of the blast be not high enough to fuse the pyrophosphate. The action, however, may easily occur if Gooch's platinum crucibles containing old precipitates be used. The action is most marked if the ignition be conducted quickly in covered crucibles.

[6] W. F. Hillebrand (*Bull. U.S. Geol. Sur.*, **700**, 151, 1919), W. M. McNabb (*Journ. Amer. Chem. Soc.*, **50**, 301, 1928), H. Neubauer (*Zeit. angew. Chem.*, **7**, 678, 1894) say the calcined pyrophosphate will be white if the precipitation be made in the presence of ammonium sulphate. When the precipitate is ignited too rapidly, there is a rapid shrinking and sintering. Particles of carbon are liable to be enclosed with the precipitate. It is then almost

It is a bad practice to remove the last trace of carbon by blasting.   The precipitate should be white before the blast is applied.   If the contents of the crucible have a dirty white appearance, Fresenius [1] recommends moistening the precipitate with a few drops of nitric acid.   Dry and ignite as before.   There is always a slight loss after the nitric acid treatment,[2] probably owing to the fact
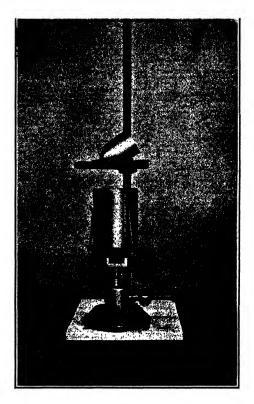
FIG. 74.—Ignition over Argand Burner.

that some $MgH_4(PO_4)_2$ is formed.   This on ignition forms magnesium meta-phosphate—$Mg(PO_3)_2$—which decomposes as indicated on page 206.   After

impossible to burn off the carbon by ignition, even in a blast (R. Bunsen; F. Muck, *Zeit. anal. Chem.*, 19, 131, 1880; S. J. Kiehl and H. B. Hardt, *Journ. Amer. Chem. Soc.*, 55, 3555, 1933).   L. L. de Koninck (*Zeit. anal. Chem.*, 29, 165, 1890) considers the frequent blackening of magnesium pyrophosphate is not due to particles of carbon derived from the filter-paper, but to the presence of organic bases (*e.g.* pyridine) in commercial ammonia and its salts.   L. A. Cuthbert, *Journ. Amer. Leather Chem. Assoc.*, 10, 459, 1915; J. G. Pereira, *Anal. Fis. Quim.*, 12, 109, 1914; S. Karaoglanoff, *Jahrb. Univ. Sofia*, 7, 1, 1910; D. Balareff, *Zeit. anorg. Chem.*, 97, 149, 1916.   K. D. Jacobs and D. S. Reynolds (*Journ. Assoc. Off. Agr. Chem.*, 11, 128, 1928) have shown that when carbon and magnesium pyrophosphate are heated together in an atmosphere of nitrogen at temperatures of 1000° to 1100°, up to 32 per cent. of the phosphorus may be volatilised in an hour.

[1] R. Fresenius, *Quantitative Chemical Analysis*, London, 2, 190, 1876.

[2] According to D. Campbell (*Chem. News*, 6, 206, 1862), the treatment of magnesium pyrophosphate with nitric acid is objectionable, because the liberated phosphoric acid may volatilise at the high temperatures required for expelling the last traces of the nitric acid. J. O. Handy, *Journ. Amer. Chem. Soc.*, 22, 31, 1900; E. Luck, *Zeit. anal. Chem.*, 13, 255, 1874.

ignition to constant weight, cool in a desiccator and weigh as $Mg_2P_2O_7$.   This weight multiplied by 0.3621 [1] gives the equivalent weight of MgO.[2]

Corrections.—Magnesia determinations are usually a little high owing to the presence of some impurities, *e.g.* lime, manganese, silica.

(*a*) *Lime.*—There is not usually sufficient magnesia present in clays to render it advisable to apply Hillebrand's correction for lime.[3] If, however, over, say, 2 per cent. of magnesia be present, the correction may be made if the work is intended to be exact.   Digest the pyrophosphate in a little dilute sulphuric acid, and add 9 to $9\frac{1}{2}$ times its volume of absolute alcohol.   After standing overnight, filter off the scarcely visible precipitate of calcium sulphate and wash it free from phosphates by means of alcohol.   Dry the precipitate; dissolve in hot water slightly acidulated with hydrochloric acid and precipitate the lime in ammoniacal solution by means of ammonium oxalate (page 202). Filter, wash, ignite and weigh as CaO.   Add the result to the lime and subtract it from the magnesium pyrophosphate.

(*b*) *Manganese.*—If this element [4] be present, it can be determined colorimetrically in the nitric acid solution of the precipitate.   In such cases evaporate the solution to dryness, drive off the ammonium salts by ignition and again evaporate the residue to dryness two or three times with nitric acid (or once with sulphuric acid) to drive off the chlorine.   Determine the manganese colorimetrically, as indicated on page 406, and deduct the corresponding weight of $Mn_2P_2O_7$ from the weight of the nominal $Mg_2P_2O_7$.

(*c*) *Silica.*—If silica be present, the magnesium pyrophosphate will leave a residue [5] when treated with dilute sulphuric acid.   This is filtered off, ignited and weighed as indicated on page 167.   The amount of silica is subtracted from the magnesium pyrophosphate.

(*d*) *Barium.*—See page 581 for barium in silicates.[6]

Errors.—Some idea of the results may be gathered from the eight independent determinations on one sample of clay:—

$$0.0106; \quad 0.0114; \quad 0.0109; \quad 0.0110; \quad 0.0107; \quad 0.0103; \quad 0.0117; \quad 0.0118$$

with a mean of 0.0110 grm. MgO, representing 1.10 per cent. of MgO.   The deviations from this value range between ± 0.08. [7]

§ 100. Determination with 8-Hydroxyquinoline ("Oxine").

The filtrate from the calcium oxalate precipitate is heated almost to boiling and made alkaline, if necessary, with a slight excess of ammonia.   A 5 per cent. alcoholic solution of 8-hydroxyquinoline, C_9H_6NOH, is then added, drop by drop, with stirring, until in slight excess, as shown by the yellow colour of the

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[1] Or by 0.6378 for the equivalent weight of P_2O_5 (page 674).

[2] M. Schmoeger, *Zeit. anal. Chem.*, **37**, 308, 1898; H. Mastbaum, *ib.*, **37**, 581, 1898.

[3] W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **700**, 152, 1919.

[4] The magnesium pyrophosphate has generally a pink colour if appreciable amounts of manganese be present.

[5] Some platinum sulphide may also be present (see page 167).

[6] B. Tollens (*Journ. Landw.*, **30**, 48, 1883) says that if basic lime or magnesia phosphates are precipitated with the ammonium magnesium phosphate, and a little silver nitrate be added, a yellow colour will be developed when the precipitate is warmed.

[7] For a colorimetric method for determining quantities of magnesium of the order of 0.1 mgrm. *via* the triple ferrocyanide of calcium, magnesium and hexamethylenetetramine, see L. Debucquet and L. Velluz, *Compt. rend.*, **196**, 2006, 1933.   For the volumetric determination of the precipitated magnesium ammonium phosphate, see F. W. Bruckmiller, *Journ. Amer. Chem. Soc.*, **39**, 610, 1917.

liquid.[1] Large excess must be avoided, since the reagent itself may be precipitated. The yellow crystalline precipitate of magnesium oxyquinolinate is filtered off through a weighed Gooch crucible, or a sintered glass filter crucible, which has been previously dried at $100°$-$105°$. The precipitate is washed free from foreign salts with hot water, made just alkaline with ammonia. The crucible and contents are dried to constant weight at $100°$-$105°$, when the precipitate loses two molecules of water of crystallisation and has the final composition, $Mg(C_9H_6NO)_2 . 2H_2O$, with 11·57 per cent. of magnesium oxide. By drying at $130°$-$140°$ the precipitate becomes anhydrous; or it may be ignited in a porcelain crucible with 2–3 grms. of anhydrous oxalic acid and weighed as magnesium oxide.

Volumetric Determination. — The washed precipitate is dissolved off the filter-paper with 5 per cent. hydrochloric acid. After well washing the paper, the filtrate and washings are diluted until about 2 per cent. of free hydrochloric acid is present. A measured excess of 0·1N-bromide-bromate solution [2] is added, followed by a few grms. of potassium iodide. The liberated iodine is titrated with 0·1N-thiosulphate solution with starch as indicator. 1 c.c. of 0·1N-bromide-bromate solution represents 0·000504 grm. MgO.

[1] R. Berg, *Zeit. anal. Chem.*, **71**, 23, 1927; F. L. Hahn and K. Vieweg, *ib.*, **71**, 122, 1927; F. L. Hahn and E. Hartlieb, *ib.*, **71**, 225, 1927; F. L. Hahn, *ib.*, **86**, 153, 1931; W. Fresenius, *ib.*, **96**, 433, 1934; R. Berg, *Journ. prakt. Chem.*, (2), **115**, 178, 1927; I. M. Kolthoff, *Chem. Weekb.*, **24**, 606, 1927; R. Strebinger and W. Reif, *Mikrochem. Pregl Festschrift*, 319, 1929; R. Berg, *ib. Emich Festschrift*, 18, 1930; F. Eichholtz and R. Berg, *Biochem. Zeit.*, **225**, 352, 1930; W. A. Hough and J. B. Ficklen, *Journ. Amer. Chem. Soc.*, **52**, 4752, 1930; E. Cattelain, *Journ. Pharm. Chim.*, (8), **11**, 484, 1930; G. Glomaud, *ib.*, (8), **19**, 14, 1934; K. Nehring, *Zeit. Pflanz. Düng.*, **21A.**, 300, 1931; H. Fredholm, *Svensk Kem. Tids.*, **44**, 79, 1932; A. Granger, *Céram. et Verrerie*, 137, 1932; H. R. Fleck and A. M. Ward, *Analyst*, **58**, 388, 1933; H. Gotô, *Journ. Chem. Soc. Japan*, **54**, 725, 1933; D. C. Vucetich, *Rev. Facultad Cienc. Quim.*, **9**, 81, 1934; H. Sheyn, *Naturaliste Canadien*, **61**, 74, 1934; M. Javillier and J. Lavollay, *Bull. Soc. chim. biol.*, **16**, 1531, 1934; R. F. R. Sykes, *Journ. Soc. Glass Tech.*, **20**, 345, 1936.

[2] BROMIDE-BROMATE SOLUTION.—Dissolve 2·7835 grms. of potassium bromate and 25 grms. of potassium bromide and dilute to 1 litre. Pure potassium bromate can be prepared by three crystallisations, and drying the last crop of crystals at $140°$—M. L. Yakowitz, *Journ. Assoc. Off. Agr. Chem.*, **18**, 505, 1935. For the use of α-naphthoflavone as indicator in bromate-bromide titrations, see R. Uzel, *Coll. Czech. Chem. Comm.*, **7**, 381, 1935.

CHAPTER XVII.

THE DETERMINATION OF THE ALKALIES.

§ 101. Meretricious Methods for Estimating the Alkalies.

1. *Difference Method.*—We shall see very shortly that the sum of the different constituents in a clay analysis may vary between 99·5 and 100·5. Assuming that the tolerated errors in the determination of the different constituents correspond with a total lying within 99·5 and 100·5, it follows that if the alkalies be determined by summing the different constituents actually determined and subtracting the result from 100, the alkalies may actually be 0·5 per cent. greater or less than the number obtained by the subtraction. This means that a clay with 1 per cent. of alkalies might be reported with $\frac{1}{2}$ or $1\frac{1}{2}$ per cent., and the numbers mean that the clay might have anything between 0·5 and 1·5 per cent. alkalies, on the assumption that the analysis has been conducted accurately. The number representing the alkalies would therefore be quite misleading unless interpreted as just indicated. It would certainly be better and more honest to report, "Alkalies not determined." It will also be noticed that when a constituent—say the alkalies—is determined by difference, and the whole analysis totals 100, there is no check on the accuracy of the analysis, and the numbers are accordingly under more or less suspicion.

2. *Calculation from the Supposed Quantities of Potash and Soda.*—There is another unsatisfactory method used for estimating the alkalies.[1] The mixed chlorides are isolated and weighed. It is then assumed that the potassium and sodium chlorides are present in equal or some other proportions. The corresponding potash and soda are then calculated by arithmetic and reported as "alkalies." This method is possibly less objectionable than the preceding one, but it too must be condemned. It pretends to represent by number a magnitude which has not really been determined.[2] There is no method known for determining alkalies without separating them into "potash and soda."

§ 102. The Separation of the Alkalies as Mixed Chlorides—Smith's Process.

The alkalies in silicates are usually determined by first decomposing the clay with hydrofluoric acid, or by fusion with bismuth, lead or boric oxide, or by sintering with calcium carbonate and ammonium chloride.[3] The constituents other than alkalies are then removed. The mixed alkali salts

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[1] At present rather too common.

[2] In illustration of both these vicious methods, see the two clay analyses, *Brit. Clayworker*, **19**, 155, 1910.

[3] E. Mäkinen (*Zeit. anorg. Chem.*, **74**, 74, 1912) fuses the silicate with calcium chloride, and otherwise proceeds as described in the text.

remain behind as a residue.[1] One of the two following methods is generally used. The most important and one of the best for general work, is that devised by J. Lawrence Smith.[2] The following are the directions:—

The Crucible and Furnace.—An ordinary covered platinum crucible may be used, but great care is then necessary not to heat the crucible at too high a temperature, nor should the crucible be heated to redness more than three-fifths of its height. The crucible recommended by Smith is best. It is a platinum crucible about 8 cm. long, 1·8 cm. wide at the mouth, and 1·5 cm. wide at the
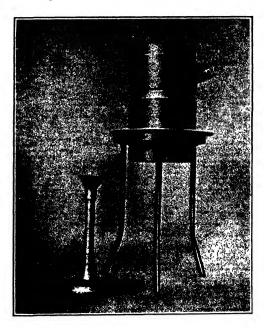
Fig. 75.—Furnace for J. L. Smith's Process.

bottom. This crucible is placed at an angle of about 45° through the side of a fireclay cylinder, and heated to the full temperature of a Bunsen burner as described below. Wrap a thin strip of asbestos paper round the crucible. This strip comes between the crucible and the fireclay jacket. It prevents the crucible jamming tightly in the aperture of the fireclay cylinder. The disposition of the fireclay cylinder and crucible is indicated in fig. 75. The source of heat is an ordinary Bunsen burner with a flat-flame nozzle (fig. 75).

Preparation of the Sample for the Decomposition.—Spread about half a gram of calcium carbonate [3] as a layer on the bottom of the crucible. Thoroughly

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[1] E. Bonjean, *Chem. News.* **80**, 240, 1899; A. Verweij, *Zeit. anal. Chem.*, **48**, 760, 1909; E. W. Dörfurt, *ib.*, **51**, 755, 1912.

[2] J. L. Smith, *Amer. J. Science*, (2), **15**, 234, 1853; (2), **16**, 53, 1853; (3), **1**, 269, 1871; *Journ. prakt. Chem.*, (1), **59**, 159, 1853; (1), **60**, 244, 1853; *Chem. News*, **23**, 222, 234, 1871; P. Holland, *ib.*, **54**, 242, 1886; F. Field, *ib.*, **1**, 193, 217, 1860; T. Döring, *Zeit. anal. Chem.*, **49**, 158, 1910. W. Pukall (*Sprechsaal*, **66**, 231, 1933; V. F. Vepritskaya and M. L. Gurevitch, *Ogneupory*, **5**, 305, 1937) recommends a mixture of lime and dihydrated calcium chloride. R. L. Steinlen (*Chem. Ztg.*, **29**, 264, 1905; B. M. Margosches, *ib.*, **29**, 385, 1905) has devised a special cooler for the lid of the crucible, to prevent loss of alkalies by volatilisation.

[3] CALCIUM CARBONATE.—This is best made by dissolving calcite in hydrochloric acid. Heat the solution of calcium chloride to boiling, and add a hot concentrated solution of

grind together in an agate mortar half a gram of ammonium chloride [1] with half a gram of the finely powdered and dried clay and 3 grms.[2] of calcium carbonate. Transfer the mixture from the mortar into the platinum crucible. "Rinse" the mortar and pestle with another gram of calcium carbonate, and transfer the rinsings to the crucible. The process of grinding the mixture and transferring it to the platinum crucible is carried out on a sheet of black glazed paper; any particles which may have been scattered in these operations are then brushed from the paper into the crucible.[3]

Ignition.— Heat the crucible, inclined as indicated above, very gently over a small flame for about 15 minutes, in order to volatilise the ammonium chloride. Then raise the temperature until the lower three-fifths of the crucible is at a dull red heat and maintain this temperature for about an hour.[4] Let the crucible cool. Beginners generally err by heating the crucible at too high [5] a temperature, when the mass vitrifies and then disintegrates with difficulty on treatment with water.[6]

Dissolution of the Cake in the Crucible.—Remove the cake from the crucible by adding 2 to 3 c.c. of water. After five or ten minutes, add more water. The sintered, not fused, cake usually comes away from the crucible quite readily. Transfer the contents of the crucible to a large porcelain or platinum dish. Cover with a clock-glass and heat the mass for about half an hour on the water

ammonium carbonate. Wash the precipitate thoroughly with hot water on a Büchner funnel (page 91), and dry. This procedure gives a dense, coarse, granular powder very suitable for this work. The calcium carbonate is generally contaminated with sodium chloride, but free from potassium chloride. This circumstance, and the fact that alkalies may be dissolved by the action of hot water on the glass vessels used in the analysis, render it necessary to find what correction must be made for the alkalies derived from the reagents and glass vessels. This is done by carrying out the whole process on 0·5 grm. of ammonium chloride and 4·5 grms. of calcium carbonate exactly as if the clay were present. This is very necessary in the analysis of highly siliceous materials with a correspondingly low alkali content. In such cases the blank from the reagents may even exceed the weight of mixed chlorides obtainable from the analysis sample itself. A blank test made in this way gave 0·00022 grm. Na$_2$O and no K$_2$O for the materials quoted in the text. See M. Gräger, *Neues Jahrb. Pharm.*, 29, 158, 1868. K. Fabich (*Verhandl. geol. Bundesanstalt*, 241, 1930; *Chem. Zentr.*, ii, 601, 1931) reports that the purest commercial samples of calcium carbonate contain from 0·00045 to 0·0316 grm. of alkali per 4 grms. of carbonate. For barium carbonate in place of calcium carbonate and ammonium chloride, see G. Werther, *Journ. prakt. Chem.*, (1), 91, 321, 1864. For the determination of sodium in calcium carbonate, see E. R. Caley, *Ind. Eng. Chem. Anal. Ed.*, 1, 191, 1929.

[1] AMMONIUM CHLORIDE.—The ammonium chloride is made by neutralising pure ammonia with pure hydrochloric acid, or by resubliming commercially pure ammonium chloride. J. S. Stas, *Œuvres Complètes*, Bruxelles, 1, 468, 1894; *Chem. News*, 15, 194, 217, 231, 1867.

[2] If the silicate contains much iron, or is liable to sinter, increase the amount of calcium carbonate.

[3] W. van Tongeren (*Zeit. anorg. allgem. Chem.*, 218, 252, 1934; *Chem. Weekb.*, 32, 224, 1935) grinds the sample and an equal weight of ammonium chloride under alcohol, then adds the calcium carbonate and continues the grinding. The mixture is dried in an air oven. This procedure is said to avoid loss of material.

[4] P. Wenger and E. Brange (*Mon. Sci.*, (5), 8, 1, 97, 1918) say that the reaction is completed by heating for 2 hours at 700°. L. Breeman, junr., and S. R. Scholes (*Bull. Amer. Cer. Soc.*, 13, 334, 1934) sinter for 45 minutes at 800°.

[5] A. Verweij (*Zeit. anal. Chem.*, 48, 760, 1909) uses a platinum crucible 4·5 cm. high and 3·5 cm. in width. He covers the mixture with a layer of 3 grms. of calcium carbonate, and after the expulsion of ammonia, heats the mixture for an hour over a Teclu or powerful Bunsen burner. The cold mass is boiled 15 minutes with water, etc. C. Prussing (*Zement*, 20, 360, 1931) finds that with gas of high thermal value, and using Teclu's burner, considerable quantities of alkalies may be lost by volatilisation.

[6] To prevent the charge from sticking, T. C. Green (*Chem. Analyst*, 16, 16, 1927) places a cork borer in the crucible and fills the space between the crucible and the borer with calcium carbonate. The mixture is then fed in through the inside of the borer.

bath with about 50 c.c. of water,[1] and restore that lost by evaporation from time to time. Triturate any large particles to powder with a small agate pestle. Decant the clear liquid through a filter-paper. Wash about four times by decantation and transfer the residue to the filter-paper. Wash until the washings only give a faint turbidity with silver nitrate.[2] If the clay has been perfectly decomposed, the residue on the filter-paper should leave no undecomposed residue when treated with hydrochloric acid.[3]

Removal of Lime.—The filtrate is heated to 80°-90° and 10 c.c. of ammonium carbonate solution [4] added to precipitate the lime. The solution is filtered and the residue well washed, the filtrate and washings being retained. A hole is made in the filter-paper, the precipitate washed through into the beaker from which it has just been filtered and redissolved in about 5 c.c. of concentrated hydrochloric acid. The solution is boiled, a slight excess of ammonia and another 10 c.c. of the ammonium carbonate solution added, and the liquid filtered into the beaker containing the first filtrate. The residue is again well washed before discarding.[5] Evaporate [6] the filtrate to dryness in a platinum or porcelain dish. Cover the dish with a clock-glass and bake for 30 minutes in an air oven at 110° to expel the last traces of moisture. Remove the ammonium salts by gentle ignition in a moving flame.[7] Moisten the cold residue with about 3 c.c. of ammonium oxalate solution [8] and a drop of ammonia in order to precipitate the last traces of lime, and, after covering with a clock-glass, allow to stand for 12 hours—say overnight.[9]

Determination of the Mixed Alkali Chlorides—Filter the liquid through a 7 cm. paper into a small platinum dish and wash the residue on the paper with a few c.c. of ammonium oxalate solution. The filtrate is evaporated to dryness on a water bath, but as the liquid may spurt during the early stages of the evaporation, the dish is covered with a clock-glass until all the ammonium salts have decomposed, and any liquid adhering to the glass is then washed back into the dish. When dry, the residue in the dish is ignited, cooled and then

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[1] According to T. Döring (*Zeit. anal. Chem.*, 49, 158, 1910), at least 500 c.c. of filtrate should be obtained per gram of sample, because the alkali chlorides are retained tenaciously by the insoluble mass.

[2] The faint turbidity is possibly due to the presence of calcium oxychlorides which are slowly dissolved from the residue. Borates will be found in the insoluble residue.

[3] Some flecks of silicic acid may separate.

[4] AMMONIUM CARBONATE SOLUTION.—100 grms. of ammonium carbonate are dissolved in 100 c.c. of concentrated ammonia (sp. gr. 0·88) and the solution diluted to 500 c.c. with water. For the reaction between alkali chlorides and ammonium carbonate, see P. Malikov and M. Rozenblatt, *Journ. Russ. Phys. Chem. Soc.*, 47, 1093, 1915.

[5] D. Köszegi (*Acta Sci. Reg. Univ. Hung. Fran. Jos.*, 2, 214, 1927) removes the lime by evaporating the filtrate to dryness with hydrochloric acid and extracting the dry residue with absolute amyl alcohol, in which sodium and potassium chlorides are practically insoluble.

[6] G. H. Bailey (*Journ. Chem. Soc.*, 65, 445, 1894) noticed a loss of alkali chlorides during the evaporation of 0·1 N-solutions of alkali chloride. For instance, lithium chloride lost 0·25 mgrm. per litre; sodium chloride, 0·81 mgrm. per litre; potassium chloride, 1·22 mgrms.; rubidium chloride, 2·95 mgrms.; and cæsium chloride, 3·35 mgrms. per litre.

[7] In specially exact work, the removal of the ammonium salts is best effected by heating the dish placed high above the flame. This requires about 45 minutes. If the ignition be conducted too rapidly, or the dish be too strongly heated, several milligrams of alkali may be lost; otherwise, A. Mitscherlich (*Journ. prakt. Chem.*, (1), 83, 459, 1861; J. Boussingault, *Compt. rend.*, 64, 1159, 1867) has shown that there is no loss of alkali during the expulsion of the ammonium salts. See page 209. If phosphates are present, ignition in a silica dish renders part of the potassium insoluble—L. D. Haigh, *Journ. Assoc. Off. Agric. Chem.*, 11, 219, 1928.

[8] If sulphates be present, first add a drop of barium chloride solution and remove the excess of barium by means of ammonium carbonate.

[9] Schaffgotsch's or Gooch and Eddy's solutions can also be used for the removal of lime and magnesia, as described in the next section.

moistened with a few drops of concentrated hydrochloric acid, again evaporated to dryness, ignited at a *low red* heat [1] until white, cooled and weighed. The residue is then washed out with hot water into a small porcelain dish and the platinum dish again ignited and weighed. The difference in weight represents the weight of the mixed—sodium and potassium—chlorides. If the residue dissolves in water, all is well. If not, filter off the insoluble matter, ignite and weigh. Deduct the weight of the insoluble residue from the weight of the total chlorides.

The Accuracy of the Results.—The following numbers represent the results obtained with eight independent determinations on half-gram samples of the same clay:—

0·0226; 0·0229; 0·0233; 0·0229; 0·0228; 0·0221; 0·0225; 0·0222

The mean value is 0·0227 grm. per half-gram of clay; the deviations range approximately ±0·0006 per half-gram of clay. There is also a constant error due to loss of alkali. J. L. Smith says: "Usually an amount of alkali remains behind amounting to 0·2 to 1·0 per cent. of the materials used." Smith recovers this by reheating the residue after the first sintering with the ammonium chloride mixture, and mixing the aqueous extract with the extract of the sintered mass obtained during the first heating. By proceeding as described above, the errors from this source will rarely exceed 0·002 grm. Holland [2] has investigated the magnitude of the loss due to the retention of alkalies by the precipitate during the first extraction. He obtained:—

Table XXXIV.—Loss of Alkalies in Smith's Process.

Nature of silicate.	Mixed chlorides, in grams.	
	First sintering.	Re-sintering of residue.
Basalt (Wales) . . .	0·1305	0·0040
Basalt (Westmoreland) . .	0·1118	0·0032
Leucite (Rieden, Germany) .	0·2472	0·0034
Red spongy lava (Pompeii) .	0·1434	0·0038
Syenite (North Wales) . .	0·1634	0·0029

Hence it is very probable that practically all but about 2 per cent. of the total alkali is extracted during the first operation. Under these conditions, about 2 per cent. of the total alkali is lost. This agrees with Dittrich's observation,

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[1] A. Mitscherlich (*Journ. prakt. Chem.*, (1), **83**, 485, 1861) has shown that a six minutes' heating to the melting-point of potassium chloride resulted in a loss of 0·0040 per cent. KCl and 0·0042 per cent. NaCl.—H. Rose, *Pogg. Ann.*, **31**, 133, 1833; G. H. Mulder, *Archiv Pharm.*, (2), **129**, 231, 1867; J. Reichmann, *Journ. Gasbeleuchtung*, **7**, 9, 1864; P. M. Delacharlonny, *Compt. rend.*, **103**, 1128, 1886; H. B. von Adlerskron, *Zeit. anal. Chem.*, **12**, 390, 1873; G. F. Smith, F. M. Stubblefield and E. B. Middleton (*Ind. Eng. Chem. Anal. Ed.*, **6**, 314, 1934) find that mixed crystals of sodium and potassium chlorides, after drying at 550°, still retain on an average 0·08 per cent. of occluded moisture. They weigh the mixed chlorides after fusion at 900° in a Lawrence Smith's crucible with its lid water-cooled, otherwise the volatilisation loss would be excessive. E. Spencer and K. B. Sen (*Analyst*, **54**, 224, 1929), by using ammonium bromide and hydrobromic acid, weigh the alkalies as mixed bromides, which are less volatile than the chlorides. For determination as iodides, see L. Szebellédy and K. Schick, *Ind. Eng. Chem. News Ed.*, **11**, 110, 1933; *Zeit. anal. Chem.*, **97**, 106, 1934; M. Hegedüs, *ib.*, **107**, 166, 1936.

[2] P. Holland, *Chem. News*, **54**, 242, 1886; T. E. Keitt, *Chemist-Analyst*, **8**, 9, 1914.

cited Table XXXVIII., page 243, and the result may be taken to represent the constant incidental to the process. The other chief errors arise from (1) too high a temperature for the sintering; (2) imperfect leaching of the sintered mass; (3) driving off the ammonium chloride too rapidly; (4) spitting by too rapidly heating to drive off the ammonium salts; (5) igniting the mixed chlorides at too high a temperature; (6) imperfect separation of magnesium and calcium salts; and (7) the presence of sulphates. If the silicate contained appreciable quantities of sulphur, this element will be found as alkali sulphates along with the chlorides. The sulphates can be converted into chlorides by adding a little barium chloride before the final precipitation of the calcium is made. The excess of barium is removed by the ammonium carbonate and oxalate treatments.[1]

§ 103. The Separation of the Alkalies as Mixed Chlorides— Berzelius' Process.

It is sometimes convenient to decompose the silicate by a mixture of sulphuric and hydrofluoric acids, as recommended by Berzelius.[2] The alumina, lime, magnesia, etc., may be precipitated by mercuric oxide,[3] barium oxide,[4] or ammonium carbonate.[5] The alkali salts remain in solution. The following plan gives good results. It is rather quicker than Smith's process, but more expensive materials are needed. The "yield" of mixed chlorides is also about 1 per cent. (on the "total alkali") higher than in Smith's process. Berzelius' process is not recommended when the silicate contains boron compounds. In Smith's process the boron remains behind as insoluble calcium borate.

Removal of Silica, Alumina and Iron.—Mix 1 grm. of the clay in a platinum crucible with 5 c.c. of concentrated sulphuric acid and add carefully, in small quantities at a time, about 20 c.c. of pure hydrofluoric acid.[6] Heat gently on a sand bath; when the hydrofluoric acid has evaporated, add another 20 c.c. of hydrofluoric acid, and heat as before. When the hydrofluoric acid has nearly

[1] For the adsorption of alkali salts by the precipitated barium sulphate, see G. Hager and J. Kern, *Landw. Versuchs. Stat.*, 87, 365, 1915; R. Otto, *Ber.*, 55B, 3434, 1922.

[2] J. J. Berzelius, *Pogg. Ann.*, 1, 169, 1824; E. A. Wülfing, *Ber.*, 32, 2214, 1899; C. Reinhardt, *Stahl Eisen*, 16, 448, 1896; W. Knopp, *Zeit. anal. Chem.*, 22, 421, 558, 1883; 18, 462, 1879; *Chem. News*, 48, 110, 1883; A. H. Low, *ib.*, 67, 185, 1893; *Journ. Anal. App. Chem.*, 6, 666, 1892; H. Schweitzer and E. Lungnitz, *Chem. Ztg.*, 18, 1320, 1894; E. C. Sullivan and W. C. Taylor, *Journ. Ind. Eng. Chem.*, 6, 897, 1914; J. C. Hostetter, *ib.*, 6, 392, 1914; E. W. Koenig, *ib.*, *Anal. Ed.*, 7, 314, 1935; O. Cantoni, *Zeit. anal. Chem.*, 67, 33, 1925; S. R. Scholes, *Journ. Amer. Cer. Soc.*, 16, 342, 1933; H. B. Knowles and J. C. Redmond, *ib.*, 18, 106, 1935; H. V. Krishnayya, *Chem. News*, 107, 100, 1913; R. F. R. Sykes, *Journ. Soc. Glass Tech.*, 20, 345, 1936. For the use of hydrofluoric and perchloric acids, see M. M. Green, *Ind. Eng. Chem.*, 15, 163, 1923; J. J. Morgan, *ib.*, 13, 225, 1921; A. Thürmer, *Chem. Ztg.*, 52, 974, 1928.

[3] E. F. Smith and P. Heyl, *Zeit. anorg. Chem.*, 7, 82, 1894; *Chem. News*, 70, 193, 204, 1894; G. Starck, *Zeit. anal. Chem.*, 48, 415, 1909.

[4] J. N. von Fuchs, *Schweigger's Journ.*, 62, 184, 1831; H. Rose, *Pogg. Ann.*, 83, 137, 1851; J. E. Thomsen, *Journ. Amer. Chem. Soc.*, 30, 420, 1908.

[5] F. G. Schaffgotsch, *Pogg. Ann.*, 104, 482, 1858; H. Weber, *Vierteljahr. prakt. Pharm.*, 8, 161, 1859. Schaffgotsch's solution is made by dissolving 230 grms. of ammonium carbonate in 180 c.c. of aqueous ammonia (sp. gr. 0·92) and making the solution up to a litre. F. A. Gooch and E. A. Eddy, *Chem. News*, 97, 280, 1908; *Amer. J. Science*, (4), 25, 444, 1908; F. A. Gooch and M. A. Phelps, *ib.*, (4), 22, 488, 1906; F. A. Gooch, *ib.*, (3), 48, 216, 1893; P. E. Browning and W. A. Drushel, *Zeit. anorg. Chem.*, 54, 151, 1907; D. Divers, *Journ. Chem. Soc.*, 61, 196, 1892; E. Bonjean, *Bull. Soc. chim.*, (3), 21, 691, 1899; *Chem. News*, 80, 248, 1899.

[6] R. Kayser (*Zeit. öffent. Chem.*, 5, 107, 1900) found 2·4 per cent. of potash in one sample, and 1·4 per cent. of potash and 0·6 per cent. soda in another sample of so-called "chemische reine Flusssäure"; see also R. G. Thin and A. C. Cumming, *Journ. Chem. Soc.*, 107, 361, 1915. Hence the necessity for testing this acid for alkalies. See pages 149 and 513.

gone, evaporate the solution to dryness. Cool. Add concentrated aqueous ammonia and heat gently. When the mass is quite disintegrated, filter and wash with hot water.

Transformation of the Sulphates into Chlorides.—It is now advisable to transform the sulphates in the filtrate into chlorides [1] by precipitation as barium sulphate, and removing the excess of barium chloride as barium carbonate [2] in the following manner:—Acidify the filtrate with hydrochloric acid,[3] and heat the solution to boiling. Add a slight excess of a hot solution of barium chloride [4] to the boiling solution. Heat the mixture to boiling and let it stand overnight. Filter, wash with hot water, evaporate the filtrate to dryness in a platinum dish, ignite to drive off the ammonium salts and cool. The barium is removed during the next operation.

Removal of Magnesia and Lime.—The main difficulty in this process is the removal of the magnesia. Ammonium magnesium carbonate is appreciably soluble in ammoniacal ammonium carbonate (Schaffgotsch's solution), and an exact separation is not possible by this reagent. Gooch and Eddy have shown that an alcoholic "Schaffgotsch's solution" is quite effective, since the precipitation of the magnesia is then complete. Add about 50 c.c. of water to the ignited residue, then add 50 c.c. of absolute alcohol and 50 c.c. of an alcoholic solution of ammonium carbonate—Gooch and Eddy's solution.[5] Stir the mixture thoroughly and let it stand about 20 minutes. Filter into a weighed platinum dish and wash with Gooch and Eddy's reagent. Dissolve the precipitate in dilute hydrochloric acid, add an excess of ammonia, and repeat the above process. Evaporate the combined filtrates to dryness. Drive off the ammonium carbonate by gentle heating. Add a few drops of concentrated hydrochloric acid and again evaporate to dryness. Ignite, cool and weigh the mixed chlorides.

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[1] According to H. Rose (*Pogg. Ann.*, **74**, 568, 1848), when alkali sulphates are mixed with ammonium chloride and exposed to a red heat, the alkali sulphate is partly, and on repeated application of the process wholly, transformed into the chloride. E. Nicholson (*Chem. News*, **26**, 147, 1872) claims that this reaction is of no use as an analytical process. According to F. C. Phillips (*Zeit. anal. Chem.*, **13**, 149, 1874; M. Chikashigé, *Chem. News*, **71**, 17, 1895), for complete conversion, the temperature of ignition should be just short of the melting-point of sodium and potassium chlorides, and the best way of converting the sulphates to chlorides is to evaporate the solution to dryness in a platinum basin with ammonium chloride. Mix the residue with dry powdered ammonium chloride and calcine to a constant weight in a covered crucible to avoid loss by volatilisation. H. Ritter (*Sprechsaal*, **63**, 506, 1930; W. Pukall, *ib.*, **66**, 231, 1933) prefers to weigh the alkalies as mixed sulphates rather than chlorides, owing to the lower volatility of the former.

[2] Better results are obtained at a later stage by working with chlorides, although some get the alkalies at the last stage as mixed sulphates instead of mixed chlorides, and determine the potassium as potassium chloroplatinate in the mixed sulphates. The small amount of sulphuric acid liberated during the double decomposition: $K_2SO_4 + H_2PtCl_6 = K_2PtCl_6 + H_2SO_4$, does not appreciably affect the results.

[3] There is a slight loss of alkali chlorides by adsorption. The barium sulphate carries down less potassium salts when the precipitation is made in feebly acid solution—B. West, *Zeit. anal. Chem.*, **20**, 357, 1881. J. F. de Vries (*Chem. Weekblad*, **5**, 261, 1908) found 26·6 instead of 27·0 per cent. K_2O. The loss was due to the potassium salt retained by the barium sulphate. See also footnote 1, page 219. R. Otto (*loc. cit.*) obtains a precipitate of barium sulphate free from adsorbed alkali salts by running the alkali sulphate solution and a solution of barium chloride, slowly and in equivalent quantities, from burettes into boiling 1·0N-hydrochloric acid.

[4] Commercial "guaranteed pure" barium chloride not infrequently contains potassium salts. Hence attention must be paid to this matter, otherwise high results may be obtained.

[5] GOOCH AND EDDY'S SOLUTION.—Mix 180 c.c. of ammonia, 800 c.c. of water, 900 c.c. absolute alcohol and saturate the mixture with ammonium carbonate. Filter off any undissolved salt.

§ 104. The Indirect Determination of Potash and Soda.

In some cases it is possible to determine, quite accurately, the potash and soda in the mixed chlorides [1] by the so-called "indirect process." The weight of the mixed chlorides is first determined, and afterwards the total chlorine by, say, Mohr's process (page 68), particularly if an adsorption indicator such as dichlorofluorescein be used. From the data so obtained, it is possible to deduce the respective amounts of soda and potash by arithmetic.

Let KCl denote the weight of potassium chloride and NaCl the weight of sodium chloride in the mixture. Let w denote the weight of the mixed chlorides, and u the weight of chlorine in the mixture. Then, obviously,

$$KCl + NaCl = w \quad . \quad . \quad . \quad . \quad (1)$$

One part by weight of sodium chloride contains 0·6066 part of chlorine, and one part by weight of potassium chloride contains 0·4756 part of chlorine. Hence the total weight of chlorine may be written:

$$0 \cdot 6066 NaCl + 0 \cdot 4756 KCl = u \quad . \quad . \quad . \quad (2)$$

These two relations suffice for the computation. Eliminate NaCl between the two equations. We thus obtain, on reduction,

$$KCl = 4 \cdot 630w - 7 \cdot 633u; \quad \text{and} \quad NaCl = w - KCl$$

by substituting the value of KCl so obtained, in the first equation. The conversion of the amounts of the two chlorides so obtained into the equivalent oxides is effected in the usual manner, namely:—

$$\text{Amount of } KCl \times 0 \cdot 6317 = \text{Amount of } K_2O$$
$$\text{Amount of } NaCl \times 0 \cdot 5302 = \text{Amount of } Na_2O$$

This method does not give good results with the small amounts of alkalies found in clays, unless very special care be taken to ensure the absence of magnesium and other metallic chlorides. Collier [2] obtained quite satisfactory results with mixtures of *pure* salts; for instance:—

Table XXXV.—Test Analyses—Indirect Separation of Potassium and Sodium Chlorides.

Taken.		Found.		Chlorine.	
KCl.	NaCl.	KCl.	NaCl.	Found.	Calculated.
0·0582	..	0·0573	0·0009	0·0278	0·0277
0·1284	0·0067	0·1284	0·0067	0·0651	0·0651
0·0967	0·0102	0·0967	0·0102	0·0522	0·0522
0·0782	0·0317	0·0783	0·0316	0·0564	0·0564
0·0305	0·0379	0·0304	0·0380	0·0375	0·0375
0·0101	0·1029	0·0104	0·1026	0·0672	0·0672
0·0065	0·1100	0·0058	0·1107	0·0699	0·0698
..	0·0590	..	0·0605	0·0360	0·0358

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[1] The method for the mixed sulphates is quite similar in principle.

[2] P. Collier, *Amer. J. Science*, (2), **37**, 344, 1865; *Chem. News*, **10**, 182, 1864; F. M. Lyte, *ib.*, **29**, 159, 1874; E. Fleischer, *ib.*, **19**, 265, 300, 1869; F. Mohr, *Lehrbuch der Titriermethode*, Braunschweig, 364, 1859; *Zeit. anal. Chem.*, **7**, 173, 1868; M. Kretschy, *ib.*, **15**, 37, 1876; H. Schiff, *Leibig's Ann.*, **105**, 219, 1858; T. Thomson, *ib.*, **20**, 205, 1836; K. List, *ib.*, **81**, 117, 1852; S. Panpushka, *Journ. Russ. Phys. Chem. Soc.*, **19**, 106, 1887; *Zeit. anal. Chem.*,

According to Virgili, the relative errors involved in the indirect processes for sodium and potassium salts are those indicated in Table XXXVI., on the assumption that pure salts are being treated.

Table XXXVI.—Relative Errors in Indirect Processes for the Determination of Soda and Potash.

| Determination. | Mixture contains | Relative error. | |
		Sodium salt.	Potassium salt.
Total chlorine in the mixed chlorides	$NaCl : KCl$ $NaCl : 10KCl$	$NaCl \pm 0\cdot018$ $NaCl \pm 0\cdot102$	$KCl \pm 0\cdot014$ $KCl \pm 0\cdot008$
Conversion chlorides into sulphates	$NaCl : KCl$ $NaCl : 10KCl$	$NaCl \pm 0\cdot021$ $NaCl \pm 0\cdot118$	$KCl \pm 0\cdot017$ $KCl \pm 0\cdot010$
Total SO_4 in the mixed sulphates	$Na_2SO_4 : K_2SO_4$ $Na_2SO_4 : 10K_2SO_4$	$Na_2SO_4 \pm 0\cdot021$ $Na_2SO_4 \pm 0\cdot118$	$K_2SO_4 \pm 0\cdot017$ $K_2SO_4 + 0\cdot010$

To illustrate the effect of impurities on the determination, suppose a mixture of potassium chloride, 0·200 grm., and sodium chloride, 0·020 grm., has 0·002 grm. of magnesium chloride as impurity, the calculated potassium and sodium chlorides (supposing that there are no analytical errors) will be respectively 0·190 grm. potassium chloride and 0·027 grm. sodium chloride, in place of 0·200 grm. and 0·020 grm. respectively. Suppose further that a similar mixture of potassium and sodium chlorides has 0·002 grm. of an inert impurity, say 0·002 grm. of magnesia. Then, under the above conditions, 0·206 grm. of potassium chloride and 0·016 grm. of sodium chloride would be obtained, in place of 0·200 grm. and 0·020 grm. respectively.

This all means that *the indirect process will give exact results with large or small amounts of the mixed chlorides only when no impurity is present.* Hence, when there are no means of establishing the purity of the mixture, and *when the alkalies appear at the end of a long series of separations, the method will not be very reliable, since the method of calculation multiplies a small trace of impurity into a relatively large error.* Some consider that the errors by the indirect process are less than the experimental errors by the direct process (*e.g.* Rose). This is probably the truth about the method with the limitations just stated.[1]

27, 160, 1888; L. W. Winkler, *Chem. Ztg.*, **24**, 816, 1900; G. Errera, *Gazz. Chim. Ital.*, **18**, 244, 1889; E. K. Landris, *Journ. Amer. Chem. Soc.*, **17**, 466, 1895; **18**, 132, 1896; G. Werther, *Journ. prakt. Chem.*, (1), **91**, 324, 1864; J. J. Berzelius, *De l'Analyse des Corps Inorganiques,* Paris, 69, 1827; J. P. Wuite, *Chem. Weekblad*, 4, 19, 1907; F. Walker, *Journ. Chem. Soc.,* **123**, 2336, 1923; W. W. Fischer, *Analyst*, **27**, 137, 1903; F. H. McCrudden and C. S. Sargent, *Journ. Biol. Chem.*, **53**, 235, 1918. A. J. Sofianopoulos (*Bull. Soc. chim.*, (4), **5**, 632, 1909) converts the mixed chlorides into fluorides. The process has not been thoroughly tested in general work. B. A. Shippy and G. H. Burrows (*Journ. Amer. Chem. Soc.*, **40**, 185, 1918) estimate the potassium and sodium from the refractive index of the solution. For a polarographic method of determination, see J. Heyrovsky, *Mikrochem.*, **12**, 25, 1932; V. Majer, *Zeit. anal. Chem.*, **92**, 321, 1933; *Chim. et Ind.*, Special No., 211, 1933.

[1] R. Fresenius, *Anleitung zur quantitativen chemischen Analyse*, Braunschweig, 441, 1863; H. Rose, *Handbuch der analytischen Chemie*, Braunschweig, **2**, 17, 1871. R. Bunsen (*Zeit. anal. Chem.*, **10**, 400, 1871) considers the indirect process a useful means of controlling the results by the direct process. J. Dennant (*Rep. Australasian Assoc.*, **2**, 385, 1890) objects.

§ 105. A General Study of Indirect Separations.

An indirect separation seems rather an attractive and speedy method of resolving the bases in a mixture, and it is not immediately apparent why the principle is not more extensively applied for determining, say, potash and soda; cobalt and nickel; lime and magnesia; lime and strontia. It is therefore necessary to study the principle in more detail. The problem may be stated in general terms:—

Given a mixture of two salts with different bases and one acid, or with different acids and one base, to find the amount of each constituent.—Let the salts have the general formulæ MA and NA; [1] and further, let the total weight of the mixture be w, and the weight of the common constituent u. It is required to find the weights of M and N in the mixture. For convenience, let x denote the weight of M and y the weight of N in a weight, w, of the mixture. Let a denote the weight of A in the salt MA, and b the weight of A in the salt NA, in the same quantity, w, of the mixture. Hence it follows:

$$(x + a) + (y + b) = w; \quad \text{and} \quad a + b = u$$

Further, it follows from the laws of chemical combination that $a : x = A : M$, and $b : y = A : N$, where A, M and N now denote the equivalent weights of the respective constituents represented by the letters. Then,

$$\frac{a}{x} = \frac{A}{M}; \quad \frac{b}{y} = \frac{A}{N}$$

These four equations suffice for the algebraic solution of the four unknowns—x, y, a, and b—from the given data. Solving these equations in the usual manner, we get

$$\frac{A}{M}x + \frac{A}{N}y = u \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (3)$$

which corresponds with equation (2) (p. 221). From the first pair of equations, we get

$$x + y = w - u \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (4)$$

Solving this equation for y, and substituting the result in the first equation, we get

$$x = \frac{M}{A} \cdot \frac{u(N + A) - wA}{N - M}; \quad \text{and} \quad y = \frac{N}{A} \cdot \frac{u(M + A) - wA}{M - N} \qquad . \qquad (5)$$

The last equation is not needed in the actual arithmetic, because it is easier to calculate y from the values of x, w and u in equation (4). These equations (5) generalise the method used on page 221 in solving a particular problem.

Conditions for Success.—Let us interpret the equations further. It is easy to see that if $u(N + A) - wA = 0$, x must be zero, and

$$\frac{u}{w} = \frac{A}{N + A}$$

This means that if, in the analysis of a mixture of, say, the alkali chlorides, we get a relation such that

$$\frac{u}{w} = \frac{35 \cdot 5}{23 + 35 \cdot 5} = \frac{35 \cdot 5}{58 \cdot 5}$$

no potassium chloride is present.

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[1] If A be bivalent, and M or N univalent, say, M_2A and N_2A, then we write $M' = 2M$ in place of M; and conversely, if A be univalent, and N or M bivalent, so that the salts are MA_2 and NA_2, we write $A' = 2A$ in place of A. In the first case, M', N' and A are chemically equivalent, and in the second case M, N and A' are chemically equivalent.

If M be less than N in magnitude, then $u(N + A)$ must be greater than wA, since, if wA were the greater, x would be negative, and negative values of x are impossible.   Consequently, we have

$$\frac{u}{w} > \frac{A}{N + A}$$

Every addition of KCl to NaCl makes the ratio $u : w$ greater than $A : N + A$; or greater than $35 \cdot 5 : 58 \cdot 5$.

When $M = N$, as is nearly the case with a mixture of cobalt and nickel salts, the indirect analysis is impossible because $M \sim N$ will then be zero, and equations (5) cannot be solved.

By rearranging the first of equations (5), and expressing the percentage amount of x in a mixture weighing w grams, we have

$$\frac{100M}{A(N - M)} \left[\frac{u(N + A) - wA}{w} \right] \text{ per cent. of M}$$

We see at a glance that the factor on the left is constant for a particular pair of salts, and that the greater the value of this factor, the greater the influence of errors in the determination of u and w on the final result.   With a mixture of potassium and sodium chlorides, the factor is $4 \cdot 04$; with magnesium and calcium sulphates, $3 \cdot 12$; and with nickel and cobalt sulphates, 244. It is thus easy to see, other things being equal, that a mixture of magnesium and calcium sulphates can be estimated more accurately than a mixture of potassium and sodium chlorides, while the indirect separation of nickel and cobalt sulphates is hopeless, because the errors in the determination are multiplied enormously.   Hence, other things being equal, the calculated values of x and y will be the more accurate—

(1) The smaller the numerical values of the equivalent weights of the constituents M and N;

(2) The greater the difference between the equivalent weights of the constituents M and N;

(3) The greater the equivalent weight of the single constituent A; and

(4) The nearer the ratio of the weights $u : w$ to the ratio of the equivalent weights $M : N$.[1]

§ 106. The Separation of Potassium as Potassium Perchlorate.

In place of the preceding process, it is usual to determine the potassium chloride separately and subtract this from the weight of the mixed chlorides. The remainder, *viz.* the weight of the sodium chloride, is multiplied by $0 \cdot 5302$ to get the equivalent amount of sodium oxide.   The process of separation which now holds the field, depends upon the conversion of the mixed chlorides into perchlorates by evaporation with a solution of perchloric acid.

Potassium perchlorate is practically insoluble in concentrated alcoholic solutions, while sodium, barium and magnesium perchlorates are soluble under the same conditions.   In 1831, Sérullas [2] proposed a method for the determination of potassium based on this property, but owing to the difficulty in getting pure perchloric acid at that time, and to some mistaken ideas on the properties

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[1] When the errors in the determination of u and w are the same.   For a more exact study of the relations between the calculated values of x and y and the experimental errors in the determination of u and w, see J. W. Mellor, *Higher Mathematics*, London, 539, 1926; and for a discussion on the indirect methods of analysis, see J. Fages y Virgili, *Die indirekten Methoden der analytischen Chemie*, Stuttgart, 1911.

[2] M. Sérullas, *Ann. Chim. Phys.*, (2), **46**, 294, 1831.

of perchloric acid, Sérullas' proposal did not get the attention it deserved. Pure solutions of perchloric acid can now be easily obtained in commerce, the principal sources of error have been investigated [1] and the method gives results superior to the hydrochloroplatinic process, and this in less time with the use of less expensive reagents. The greater simplicity of the process also renders it less liable to error when once the manipulation is mastered. The details of the method used in the separation are as follows:—

The Process.—Dissolve the mixed chlorides [2] in from 10 to 15 c.c. of hot water, and then add two or three times as much perchloric acid as is theoretically required to form the mixed perchlorates. [3] Evaporate the mixture, in an atmosphere free from ammonia fumes, on a water bath in a porcelain basin [4] to a syrupy liquid until fumes of perchloric acid begin to appear; cool a little. Take up the mass with hot water and add 5 to 6 c.c. of perchloric acid. Re-evaporate until the fumes of perchloric acid again begin to appear. [5] The object of this treatment is to remove the hydrochloric acid and to ensure the

[1] T. Schloesing, *Compt. rend.*, **73**, 1269, 1871; K. Kraut, *Zeit. anal. Chem.*, **14**, 152, 1875; A. Bertrand, *Monit. Scient.*, (3), **2**, 961, 1881; L. Grandeau, *Traité d'analyse des matières agricoles*, Paris, **1**, 419, 1897; D. A. Kreider, *Chem. News*, **73**, 8, 17, 1896; **72**, 241, 251, 261, 1895; *Zeit. anal. Chem.*, **9**, 343, 1870; J. E. Breckenridge, *Zeit. anorg. Chem.*, **13**, 161, 1897; *Chem. News*, **74**, 227, 1896; F. S. Shiver, *ib.*, **79**, 269, 281, 1899; *Journ. Amer. Chem. Soc.*, **21**, 33, 1899; R. Caspari, *Zeit. angew. Chem.*, **6**, 68, 1893; *Zeit. anal. Chem.*, **36**, 709, 1897; V. Schenke, *Landw. Ver. Stat.*, **47**, 36, 1896; C. Aumann, *ib.*, **60**, 231, 1901; A. Strigel and J. Dodt, *ib.*, **78**, 179, 1912; V. Schenke and P. Krüger, *ib.*, **67**, 145, 1907; W. Wense, *Zeit. angew. Chem.*, **4**, 691, 1891; **5**, 233, 1892; H. Kolbe, *Journ. prakt. Chem.*, (2), **5**, 93, 1872; F. Hamel, *Chem. News*, **26**, 27, 1872; H. Precht, *International Cong. App. Chem.*, **7**, i, 146, 1909; G. Surr, *Min. Eng. World*, **36**, 605, 1912; W. A. Davis, *Chem. World*, **1**, 219, 1912; *Journ. Agric. Soc.*, **5**, 58, 1912; *Journ. Chem. Soc.*, **107**, 1678, 1915; C. S. Piper, *Proc. Austral. Chem. Inst.*, **4**, 18, 1937; A. Vityn, *Zhur. Optyu. Agron.*, **13**, 192, 1913; F. Montanari, *Staz. Experim. Agrar. Ital.*, **33**, 454, 1900; C. Scholl, *Journ. Amer. Chem. Soc.*, **36**, 2085, 1914; G. P. Baxter and M. Kobayashi, *ib.*, **39**, 249, 1917; **42**, 735, 1920; G. P. Baxter and F. E. Rupert, *ib.*, **42**, 2046, 1920; G. F. Smith, *ib.*, **45**, 2072, 1923; G. F. Smith and J. F. Ross, *ib.*, **47**, 774, 1020, 1925; G. F. Smith and A. C. Sheard, *ib.*, **54**, 1722, 1932; G. F. Smith and J. L. Gring, *ib.*, **55**, 3957, 1933; R. G. Thin and A. C. Cuming, *Journ. Chem. Soc.*, **107**, 361, 1915; F. S. Hawkins and J. R. Partington, *ib.*, 1397, 1927; B. Schulze, *Landw. Versuchs-Stat.*, **88**, 397, 1916; G. Hager and J. Kern, *ib.*, **87**, 365, 1915; T. D. Jarrell, *Journ. Assoc. Off. Agric. Chem.*, **1**, 29, 1915; F. Pilz, *Zeit. landw. Ver.-wesen Oester.*, **18**, 77, 1915; F. A. Gooch and G. R. Blake, *Amer. Journ. Sci.*, (4), **44**, 381, 1917; D. U. Hill, *ib.*, (4), **40**, 75, 1915; S. B. Kurizian, *Proc. Iowa Acad. Sci.*, **24**, 547, 1917; R. L. Morris, *Analyst*, **45**, 349, 1920; **48**, 250, 1923; H. Atkinson, *ib.*, **46**, 354, 1921; S. J. Watson, *ib.*, **47**, 285, 1922; J. J. Morgan, *Journ. Ind. Eng. Chem.*, **13**, 225, 1921; M. M. Green, *ib.*, **15**, 163, 1923; M. Górski, *Przemysl Chem.*, **6**, 311, 1922; W. Strecker and A. Jungck, *Zeit. anal. Chem.*, **63**, 161, 1923; A. Vürtheim, *Chem. Weekb.*, **22**, 138, 1925; J. H. Yoe, *Ann. Chim. anal.*, (2), **7**, 193, 1925; A. T. Dalsgaard, *Dansk. Tids. Farm.*, **2**, 257, 1928; H. B. van Valkenburgh and W. B. McDaniels, *Journ. Colo.-Wyo. Acad. Sci.*, **1**, 44, 1930; J. d'Ans and Th. Kanakowsky, *Angew. Chem.*, **47**, 583, 1934; T. Kato, *Journ. Electrochem. Assoc. Japan*, **3**, 276, 1935. For a bibliography on the determination of potassium, see S. N. Rozanov, *Kalii* (U.S.S.R.), **4**, 27, 1933.

[2] Freed from sulphates by evaporation with a solution of barium hydroxide—W. A. Davis, *Journ. Chem. Soc.*, **107**, 1678, 1915.

[3] The amount is calculated as follows: Assume that the mixed chlorides are all sodium chloride, and that the perchloric acid used is 20 per cent. (sp. gr. 1·12) solution. Multiply the weight of the mixed chlorides by 9, and the product represents the number of cubic centimetres of acid theoretically required for the work. Perchloric acid of approximately 60 per cent. strength has a specific gravity of 1·54; 30 per cent., 1·20; and 20 per cent., 1·12. There is no difficulty about keeping the acid. It is not decomposed by hydrochloric or by sulphurous acid. The acid slowly volatilises at 138° without decomposition. It is not affected by exposure to light. The strength of the acid is easily determined by titration of a known amount with standard sodium hydroxide with phenolphthalein as indicator.

[4] Perchloric acid has a distinct solvent action on glass—F. A. Gooch and G. R. Blake, *Amer. Journ. Sci.*, (4), 381, 1917.

[5] Some prefer to evaporate to dryness at this stage.

complete conversion of the chlorides into perchlorates. This is important. Stir the cold mass with about 20 c.c. of alcohol wash liquor.[1] Keep the potassium perchlorate as coarsely granular as possible. Let settle.[2] Decant through a dried and weighed Gooch crucible. Wash the residue by decantation through the Gooch crucible three times. About 20 c.c. of the wash liquor will be needed for the washing. Transfer the precipitate to the Gooch crucible by means of the wash liquor.[3] Some prefer to wash the residue at this stage with 20 c.c. of a mixture of equal parts of 97 per cent. alcohol and ether. Dry the precipitate at 120° to 130° for about half an hour,[4] and then weigh as $KClO_4$.[5]

Calculations.—Assume that 0·5 grm. of clay has been treated by Smith's process and that 0·0243 grm. of the mixed chlorides has been obtained.

Crucible and perchlorate	6·7223 grms.
Empty crucible	6·6951 grms.
Potassium perchlorate	0·0272 grm.

Multiply the weight of the potassium perchlorate by 0·5381 in order to find the equivalent amount of potassium chloride. Hence

$$0·0272 \times 0·5381 = 0·0146 \text{ grm. of potassium chloride}$$

Multiply the weight of the potassium perchlorate by 0·33992 in order to find the equivalent amount of potassium oxide—K_2O. Hence

$$0·0272 \times 0·34 = 0·0092, \text{ or } 1·84 \text{ per cent. of } K_2O$$

Subtract the weight of the potassium chloride from the weight of the mixed chlorides, and the result represents the weight of the sodium chloride.

Mixed chlorides	0·0243 grm.
Potassium chloride	0·0146 grm.
Sodium chloride	0·0097 grm.

Multiply the weight of the sodium chloride by 0·5302 in order to find the equivalent amount of sodium oxide—Na_2O. Thus

$$0·0097 \times 0·530 = 0·0052; \text{ or } 1·04 \text{ per cent. } Na_2O$$

The Results.—The perchlorate process does its work fairly well in the presence of sulphates. Consequently it is not always necessary to remove the sulphates by means of barium chloride (page 219). Thus, with a mixture of potassium chloride and sulphate containing the equivalent of 0·0307 K_2O, Davis found

$$K_2O \ . \ . \ . \ 0·0305; \ 0·0312; \ 0·0305; \ 0·0306; \ 0·0307;$$

and with 0·1 grm. K_2SO_4 containing 0·0541 grm. K_2O, Davis obtained 0·0536 and 0·0536 grm. K_2O. Quite correct results were also obtained with potassium chloride mixed with twice its own weight of sodium chloride, sodium phosphate,

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[1] ALCOHOL WASH LIQUOR.—970 c.c. of absolute alcohol, 10 c.c. of perchloric acid (sp. gr. 1·12) and 20 c.c. of water. This solution contains 0·25 per cent. by weight of perchloric acid.

[2] The addition of a drop of ether aids filtration—E. Murmann, *Oester. Chem. Ztg.*, 13, 227, 1910.

[3] A few drops of the filtrate, evaporated to dryness on platinum foil, should show no residue. There is a slight loss due to solution of the potassium perchlorate in the wash liquor. This, R. G. Thin and A. G. Cumming (*Journ. Chem. Soc.*, 107, 361, 1915) propose to overcome by the use of a wash liquor consisting of 95 per cent. alcohol, freshly saturated with potassium perchlorate.

[4] Potassium perchlorate does not decompose below 400°.

[5] For the recovery of perchloric acid from the residues, see A. Vürtheim, *Chem. Weekblad*, 14, 986, 1917, but beware of explosions—E. Deiss, *Zeit. anal. Chem.*, 107, 8, 1936.

calcium chloride, or barium chloride.   If phosphoric acid be present,[1] a larger excess of perchloric acid is needed for the precipitation.   Small amounts of magnesia do no particular harm, provided it is not present as sulphate when the precipitation is made; large amounts of magnesium salts give high results, and they must accordingly be first removed.[2] Ammonium salts, if present, should be removed by boiling with sodium hydroxide, owing to the sparing solubility of ammonium perchlorate.

Tollert [3] has proposed the use of perrhenic acid, $HReO_4$, in place of perchloric acid.   The method is analogous to the perchlorate process, but the advantages claimed are: (1) less reagent is needed, (2) perrhenic acid is non-volatile, (3) the molecular weight of the salt (289·41) is advantageous.   The rhenium is recovered by reduction in hydrogen.

Various chemists [4] have advocated the separation of potassium from sodium as potassium hydrogen tartrate, which is weighed as such or determined volumetrically.

§ 107. The Properties of Sodium and Potassium Chloroplatinates.

This process of separation depends upon the facts: (1) that a mixture of sodium and potassium chlorides in contact with a solution of hydrochloroplatinic acid—H_2PtCl_6—forms both sodium and potassium chloroplatinates; [5] and (2) there is a marked difference in the solubility of the two salts in alcoholic solution.[6]

Solubilities of Sodium and Potassium Chloroplatinates in Alcoholic Solutions. —Both sodium and potassium chloroplatinates are appreciably soluble in water.   The solubilities of sodium and potassium chloroplatinates in different proportions of ethyl and methyl alcohols and water are indicated by the graphs, figs. 76, 77.[7] These results show that the greater the concentration of the alcohol, the less the solubility of the chloroplatinate, and that the potassium salt is less soluble in ethyl than in methyl alcohol.

Different investigators have different ideas as to the best strength of the alcoholic solution, and we find numbers ranging from 70 to 100 per cent.

[1] For the determination of potassium oxide in the presence of an excess of phosphoric acid, see C. M. Bible, *Ind. Eng. Chem. Anal. Ed.*, **4**, 234, 1932.

[2] For the determination in the presence of large amounts of sodium and magnesium salts, see A. H. Bennett, *Analyst*, **41**, 165, 1916; *Chem. Trade Journ.*, **61**, 553, 1917; and in the presence of iodides, F. S. Hawkins and J. R. Partington, *Journ. Chem. Soc.*, 1397, 1927.

[3] H. Tollert, *Naturwiss.*, **18**, 849, 1930; *Zeit. anorg. allgem. Chem.*, **204**, 140, 1932.

[4] A. Bayer, *Chem. Ztg.*, **17**, 686, 1893; F. Marshall, *ib.*, **38**, 585, 615, 1914; K. Okada, *Mem. Coll. Sci. Kyoto*, **1**, 89, 1914; H. Bokemüller, *Chem. Zentr.*, (2), 764, 1918; G. Ajon, *Giorn. Chim. Ind. Appl.*, **2**, 422, 1920; St. Minovici and C. Kollo, *Bul. Soc. chim. România*, **3**, 17, 1921; R. Meurice, *Ann. Chim. anal. Chim. appl.*, (2), **7**, 161, 1925: **8**, 129, 1926; Touaritske and Slezak, *Zhur. Sakhar. Prom.*, **2**, 462, 1928; L. Clarke and J. M. Davidson, *Ind. Eng. Chem. Anal. Ed.*, **3**, 324, 1931; E. Borsche, *Mitt. Kali-Forschungsanst.*, 61, 1920; *Chem. Zentr.*, (1), 149, 1927; *Kali*, **14**, 275, 303, 358, 374, 1920; Y. I. Chernyaeva and R. V. Krasnovskaya, *Journ. Chem. Ind. (Moscow)*, **10**, No. 10, 57, 1933; J. Kunz, *Helv. Chim. Acta*, **16**, 259, 1933; K. Scheringa, *Chem. Weekb.*, **30**, 598, 1933; W. Daubner, *Angew. Chem.*, **49**, 830, 1936.   For the determination of potassium with dipicrylamine (hexanitrodiphenylamine), see A. Winkel and H. Maas, *Angew. Chem.*, **49**, 827, 1936; for a micro- (colorimetric) process as picrate, see E. R. Caley, *Journ. Amer. Chem. Soc.*, **53**, 539, 1931.

[5] Also called platinichlorides, not platinochlorides.

[6] It is assumed that the chloroplatinic acid is free from impurities, *e.g.* nitrosylplatinic chloride (page 235).   According to A. A. Knox (*Pot. Gaz.*, **38**, 1392, 1913), R. R. Tatlock calls the purity of the platinum salt "the keystone of the process."

[7] M. Péligot, *Monit. Scient.*, (4), **6**, 872, 1892; H. Precht, *Chem. Ztg.*, **20**, 209, 1896; R. Bunsen and G. Kirchhoff, *Pogg. Ann.*, **113**, 337, 1861; E. H. Archibald, W. G. Wilcox and B. G. Buckley, *Journ. Amer. Chem. Soc.*, **30**, 747, 1908.

alcohol[1] recommended for the washing. If we were guided only by the solubility, we should recommend the use of absolute alcohol. But the Ver-
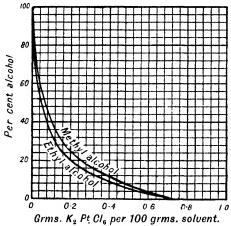
Fig. 76.—Potassium Chloroplatinate
(Archibald, Wilcox and Buckley).
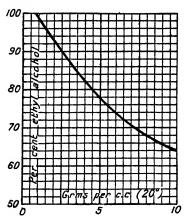
Fig. 77.—Sodium Chloroplatinate
(Péligot).

suchstationen at Halle and Darmstadt[2] have shown that alcohol of greater concentration than 96 per cent. gives too high results.

Decomposition of Sodium Chloroplatinate by Concentrated Alcoholic Solutions. —Morozewicz[3] claims to have traced the high results with concentrated alcohol to the decomposition of part of the sodium chloroplatinate, by alcohol of greater concentration than 90 per cent., into sodium chloride[4] and soluble platinic chloride; and a three- or four-fold excess of the hydrochloroplatinic acid is needed to prevent the dissociation of the sodium chloroplatinate. The presence of the insoluble cubic crystals of sodium chloride intermixed with the potassium chloroplatinate is supposed to explain the high results obtained when the alcohol used for the washing is too concentrated. There is no danger of the

[1] H. Precht (*Zeit. anal. Chem.*, 18, 509, 1879; H. Precht, H. Vogel and H. Haefcke, *Landw. Ver. Stat.*, 47, 97, 1896) recommends absolute alcohol. R. Finkener (*Pogg. Ann.*, 129, 637, 1866) and D. Lindo (*Chem. News*, 44, 77, 86, 97, 129, 1881), 98 per cent. alcohol; the Stassfurter Kaliindustrie, 96 to 100 per cent.; B. Sjollema (*Chem. Ztg.*, 21, 739, 1897), 90 per cent. alcohol; and A. Atterberg (*Zeit. anal. Chem.*, 36, 314, 1897; *Chem. Ztg.*, 22, 523, 538, 1898), 80 per cent. alcohol. H. Fresenius (*Chem. Ztg.*, 34, 1032, 1910) states that 70 per cent. alcohol gives too low results, 85 per cent. too high; and 80 per cent. alcohol gives correct results. According to H. C. Moore and R. D. Caldwell (*Journ. Ind. Eng. Chem.*, 12, 1188, 1920), 80 per cent. alcohol gives low results.

[2] *Landw. Ver. Stat.*, 45, 374, 1894; 46, 181, 1895. For the reduction of chloroplatinates, due to the presence of traces of acetaldehyde in the alcohol used, see C. G. Makris, *Journ. Pharm. Chim.*, (8), 13, 569, 1931; H. Strebinger and H. Holzer, *Zeit. anal. Chem.*, 90, 81, 1932.

[3] J. Morozewicz, *Ber. Acad. Sciences Cracovie*, 796, 1906. F. P. Treadwell (*Kurzes Lehrbuch der analytischen Chemie*, Leipzig, 2, 38, 1911) does not think that the sodium chloroplatinate is decomposed in the manner stated by Morozewicz. W. A. Davis (*Chem. World*, 1, 219, 1912) agrees with Morozewicz.

[4] F. Röttger and H. Precht (*Ber.*, 18, 2076, 1885) show that, at 15°, 100 grms. of alcohol dissolve the following amounts of sodium and potassium chlorides:—

Alcohol	.	.	.	.	.	90	92·5	95	per cent.
Sodium chloride	.	.	.	.	0·345	0·223	0·146	grm.
Potassium chloride	.	.	.	0·073	0·043	0·028	grm.

Compare D. McIntosh, *Journ. Phys. Chem.*, 7, 350, 1903; C. A. L. de Bruyn, *Zeit. phys. Chem.*, 10, 782, 1892; P. Rohland, *Zeit. anorg. Chem.*, 18, 327, 1898.

formation of sodium chloride with 80 per cent. alcohol, but another danger arises, owing to the solubility of the potassium chloroplatinate in the alcohol.[1] This means that 0·0001 grm. of potassium chloride, or 0·000063 grm. of potassium oxide, must be added to the final result for every 10 c.c. of 80 per cent. alcohol which comes in contact with the precipitate.[2] As a rule, less than 50 c.c. of the alcoholic solution are used in clay analyses, and in consequence the solubility correction may usually be neglected.[3]

Effect of the Concentration of the Solution on Precipitated Potassium Chloroplatinate.—We now inquire: should the hydrochloroplatinic acid be added to a concentrated or to a dilute solution of the two chlorides? Fresenius[4] recommends a concentrated solution. In this case, a fine pulverulent precipitate is formed, which appears under the microscope to be a mixture of stellate groups of crystals with a few octahedral crystals. If the hydrochloroplatinic acid be added to a dilute solution, subsequently evaporated down, the crystals are mainly octahedral. In both cases the crystals belong to the cubic system. Those formed in concentrated solution appear to be octahedra distorted into rod-like crystals. The crystals formed in concentrated solution also contain a relatively large number of cavities, which enclose minute globules of the mother liquid, while the octahedral crystals contain, as a rule, comparatively few inclusions. These facts are rather important. The crystals with the liquid inclusions must give high results, since the resulting precipitate contains potassium chloroplatinate plus mother liquid. The crystals can be more or less perfectly dried, but the result will then still be high, presumably owing to the residue left on evaporation of the liquid to dryness. Difficulties are also encountered in drying the potassium chloroplatinate formed in concentrated solutions. This is exemplified by the following experiment, due to Winton.[5] In one case, a mixture of 1·018 grms. of potassium chloride and 0·541 grm. of sodium chloride was made up to 100 c.c.; and in another case, a mixture of 13·063 grms. of potassium chloride and 0·541 grm. of sodium chloride was also made up to 100 c.c. Corresponding volumes were treated with hydrochloroplatinic acid. The resulting precipitates were treated in the same way, and their weights, after drying for the periods and at the temperatures stated in Table XXXVII., are shown therein.

[1] According to Péligot, the solubility of the potassium chloroplatinate is rather less in methyl alcohol (but see fig. 76), and, in consequence, some recommend the use of methyl alcohol in place of ordinary ethyl alcohol. P. Rohland (*Zeit. anorg. Chem.*, **15**, 412, 1897; **16**, 306, 1898; *Zeit. anal. Chem.*, **49**, 358, 1910) points out that methyl alcohol has additional advantages. If the precipitation be made in the presence of barium chloride, the barium chloroplatinate is liable to decompose into barium chloride and platinic chloride. The former is fairly soluble in methyl alcohol (78 parts of absolute methyl alcohol, at 15°, dissolve 1 part of barium chloride), and practically insoluble in ethyl alcohol even at 80 per cent. concentration. After washing in methyl alcohol Rohland finishes off by washing with ether. The potassium chloroplatinate is less soluble in a mixture of alcohol and ether than in alcohol alone, and R. Finkener (*l.c.*) recommends a mixture of absolute alcohol and ether in the proportions 2 : 1, while B. C. Corenwinder and G. Contamine (*Compt. rend.*, **89**, 907, 1879) recommend a mixture of 95 per cent. alcohol with ether in the proportions 9: 1; and H. N. Warren (*Chem. News*, **75**, 256, 1897) recommends a mixture of amyl alcohol and ether. G. Meillière (*Journ. Pharm. Chim.*, (7), **7**, 281, 1913) uses acetone, which is said to obviate the inclusion of sodium.

[2] The volume is easily measured if the filtration be conducted in a Gooch crucible in a Witt's filtration jar, containing a measuring cylinder. The measurement, however, need be only approximate.

[3] H. Fresenius and P. H. M. P. Brinton, *Zeit. anal. Chem.*, **50**, 21, 1911; F. Marshall, *Chem. Ztg.*, **38**, 585, 615, 1914.

[4] R. Fresenius, *Zeit. anal. Chem.*, **16**, 63, 1877; **21**, 234, 1882.

[5] A. L. Winton, *Journ. Amer. Chem. Soc.*, **17**, 453, 1895; R. Ruer, *Chem. Ztg.*, **20**, 270, 1896; F. T. B. Dupré, *ib.*, **20**, 305, 1896.

The Drying of Potassium Chloroplatinate.—Obviously, a more protracted drying at a relatively high temperature is needed to dehydrate crystals formed in a concentrated solution, than when the crystals are formed in a dilute solution. This result also explains how different investigators have made different recommendations at this stage of the analysis. Fresenius, for example, says that 30 hours at 130° are needed, while Eggertz and Nilson say that from 10 minutes to 4 hours suffice.[1]

Table XXXVII.—*Effect of Drying Potassium Chloroplatinate precipitated in Dilute and in Concentrated Solutions.*

Temperature of oven. °C.	Hours drying.	Precipitated in dilute solution.	Precipitated in concentrated solution.
100	2	99·57	100·22
100	8	99·57	100·03
100	14	99·57	99·95
100	20	99·56	99·93
130	26	99·56	99·80
130	38	99·55	99·70
130	66	99·55	99·67
160	84	99·52	99·56
160	102	99·51	99·50

The "Atomic Weight" of the Platinum in Potassium Chloroplatinate.—The older analysts used the number 197 for the atomic weight of platinum, whereas the current (1938) value is 195·23. The former number gives the factor 0·3056 for converting the weight of the potassium chloroplatinate into potassium chloride, while the later number gives the factor 0·3067. The "wrong" number apparently gives a result nearer the truth,[2] unless certain modifications be made in the conduct of the analysis (page 247).

The Transformation of Potassium Chloroplatinate into Metal before Weighing. —Owing to possible errors arising from the contamination [3] of the potassium chloroplatinate when precipitated in contact with barium chloride, as is necessary in some special cases, some reduce [4] the chloroplatinate to metal,

[1] R. Fresenius, *l.c.*; C. G. Eggertz and L. F. Nilson, *Königl. Land. Akad. Hand. Tids.'* **35,** 326, 1898; G. Krause, *Archiv Pharm.*, (3), **2,** 407, 1874.

[2] See A. Vürtheim (*Chem. Weekblad*, **17,** 637, 1920) for the composition of potassium chloroplatinate. M. McCurdy (*Proc. Trans. Nova. Scot. Inst. Sci.*, **16,** 142, 1927) ignites the separated potassium chloroplatinate at a high temperature and from the weight of platinum calculates the weight of potassium oxide. See also Horsch, *Compt. rend.*, **168,** 167, 1919.

[3] A. Atterberg, *Chem. Ztg.*, **21,** 261, 1897; *Zeit. anal. Chem.*, **36,** 214, 1897; L. Tietjens and Apel, *ib.*, **36,** 315, 1897; A. H. Allen, *B.A. Rep.*, 24, 1876; *Chem. News*, **35,** 259, 268, 1877; **36,** 17, 38, 47, 1877; E. W. Hilgard, *Zeit. anal. Chem.*, **32,** 184, 1893; H. Haefcke, *Chem. Ztg.*, **20,** 88, 1896; A. Atterberg, *ib.*, **20,** 131, 1896; H. Precht. *ib.*, **20,** 209, 1896; A. Prager, *ib.*, **20,** 269, 1896; R. Ruer, *ib.*, **20,** 270, 1896; E. Bauer, *ib.*, **20,** 270, 1896; F. T. B. Dupré, *ib.*, **20,** 305, 1896; J. H. Vogel and H. Haefcke, *Landw. Ver. Stat.*, **47,** 97, 1896.

[4] With hydrogen gas (R. Finkener, *Pogg. Ann.*, **129,** 637, 1866); zinc dust (J. Diamant, *Chem. Ztg.*, **22,** 99, 1898); mercury (E. Sonstadt, *Journ. Chem. Soc.*, **67,** 984, 1895); magnesium ribbon (L. L. de Koninck, *Zeit. anal. Chem.*, **12,** 137, 1873; **21,** 406, 1882; C. Fabre, *Compt. rend.*, **122,** 1331, 1896; A. Villiers and F. Berg, *Bull. Soc. chim.*, (3), **9,** 602, 1893; A. Fiechter, *Zeit. anal. Chem.*, **50,** 629, 1911; R. Trnka, *ib.*, **51,** 103, 1912; A. Atterberg, *ib.*, **51,** 483, 1912; W. B. Hicks, *Journ. Ind. Eng. Chem.*, **5,** 650, 1913; A. Roussin, *Bull. Soc. chim.*, (3), **9,** 602, 1893; W. N. Hartley, *Chem. News*, **14,** 73, 1866); mercurous chloride (A. Mercier, *Bull. Assoc. Belg. Chem.*, **10,** 403, 1897); formic acid (H. N. Warren, *Chem.*

wash out the soluble salts, and multiply the weight of the metal by the necessary factor to get the equivalent potassium chloride or oxide. The chlorine may also be determined in the soluble salts by titration according to Volhard's or Mohr's process (pages 65 and 68), and the result calculated to potassium chloride or oxide.[1] These methods are not usually employed in silicate analyses.

§ 108. The Separation of Potassium as Potassium Chloroplatinate.

Precipitation of Potassium Chloroplatinate.—Treat a dilute solution of the mixed chlorides in a small porcelain basin with 0·3 c.c. more than the calculated amount [2] of hydrochloroplatinic acid.[3] Evaporate the solution [4] to a syrupy

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News, **75**, 256, 1897); sodium formate (R. Böttger, *Zeit. anal Chem.*, **13**, 176, 1874; F. Jean and J. A. Trillat, *Bull. Soc. chim.*, (3), **7**, 228, 1892; B. C. Corenwinder and G. Contamine, *Compt. rend.*, **89**, 907, 1879; Woussen, *Ann. Agronom.*, **13**, 431, 1888; T. Steel, *Analyst*, **43**, 348, 1918); calcium formate (L. L. de Koninck, *Chem. Ztg.*, **19**, 901, 1895); sodium oxalate (F. Mohr, *Zeit. anal. Chem.*, **12**, 137, 1873); thioacetic acid (A. Atterberg, *Zeit. anal. Chem.*, **36**, 314, 1897; *Chem. Ztg.*, **22**, 522, 538, 1898); soap (H. Bornträger, *Zeit. anal. Chem.*, **32**, 188, 1893).

[1] J. Diamant, *Chem. Ztg.*, **22**, 99, 1898; A. Atterberg, *ib.*, **22**, 522, 538, 1898; L. L. de Koninck, *Zeit. anal. Chem.*, **35**, 72, 1896; F. Mohr, *ib.*, **12**, 137, 1873.

[2] Sufficient hydrochloroplatinic acid should be added to convert both the sodium and the potassium chlorides into the corresponding chloroplatinates. The solution of hydrochloroplatinic acid should contain 0·1 grm. of platinum per c.c. Assume that the mixed chlorides are all sodium chloride, multiply their weight by 17, and add 0·3 to the product. The result represents the number of cubic centimetres of the hydrochloroplatinic acid solution to be used. In the previous example (page 218), 0·0227 × 17 = 0·386 c.c.; and 0·386 + 0·3 = 0·7 c.c. nearly. If sufficient hydrochloroplatinic acid has been added, a drop of the solution, under the microscope, will show golden yellow octahedral crystals of potassium chloroplatinate and orange-coloured needles of sodium chloroplatinate. If colourless cubes of sodium or potassium chloride be present, insufficient hydrochloroplatinic acid has been added. The hydrochloroplatinic acid should be free from potassium and ammonium chloroplatinates. Potassium chloroplatinate is appreciably soluble in ammonium chloride (0·0015 grm. of potassium chloroplatinate dissolves in 10 c.c. of ammonium chloride solution). The importance of using pure hydrochloroplatinic acid has been emphasised by H. Vogel and H. Haefcke (*Landw. Ver. Stat.*, **47**, 97, 1896), H. Precht (*Zeit. anal. Chem.*, **18**, 509, 1879), A. F. Holleman (*Chem. Ztg.*, **16**, 35, 1892), and C. R. Fresenius (*Zeit. anal. Chem.*, **33**, 358, 1894). S. Zuckschwerdt and B. West (*Zeit. anal. Chem.*, **20**, 185, 1881) state that potassium chloroplatinate is soluble in hydrochloroplatinic acid, and consequently, if too great an excess of this acid be present, low results will be obtained. An excess, however, must be added to ensure complete precipitation. The comparatively small excess usually added cannot have an appreciable influence, even accepting Zuckschwerdt and West's data (100 c.c. of a solution of hydrochloroplatinic acid containing 7 grms. of platinum per 100 c.c. dissolve 0·3250 grm. of potassium chloroplatinate in 30 hours). W. Dittmar and J. McArthur (*Trans. Roy. Soc. Edin.*, **33**, ii. 561, 1887; *Journ. Soc. Chem. Ind.*, **6**, 799, 1887; R. R. Tatlock, *Chem. News*, **30**, 71, 1874; **43**, 273, 1881) state that "the precipitate of potassium chloroplatinate has a remarkable tendency to carry down platinum chiefly as hydroxide, if produced in the absence of a large excess of hydrochloroplatinic acid." There appears to be a kind of hydrolysis in the dilute solution. For objections to sulphates with the "platinum chloride," see A. F. Holleman, *Chem. Ztg.*, **16**, 35, 1892; B. Turkus, *Ann. Chim. anal.*, **22**, 101, 1917.

[3] G. F. Smith and A. C. Shead (*Journ. Amer. Chem. Soc.*, **53**, 947, 1931) separate from sodium and lithium by precipitating with twice recrystallised lithium chloroplatinate, Li$_2$PtCl$_6$.6H$_2$O, prepared from lithium carbonate and hydrochloroplatinic acid. The same authors also recommend (*Journ. Amer. Chem. Soc.*, **54**, 1722, 1932) weighing sodium and potassium as mixed perchlorates and then precipitating the potassium as chloroplatinate. By this method small amounts of potassium can be determined in the presence of relatively large quantities of sodium. See also G. F. Smith and J. L. Gring, *Journ. Amer. Chem. Soc.*, **55**, 1722, 1933.

[4] Sufficient water should be present to form a clear solution when first heated on the water bath.

consistency[1] on a water bath[2] in an atmosphere from which ammonia fumes are rigorously excluded.[3]   Cool.   The mass should form a solid cake.
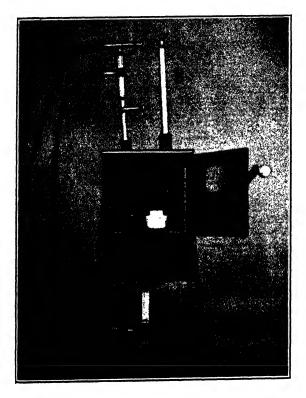
Fig. 78.—Air Bath and Thermostat.

Filtration and Washing.—Treat the residue with a few cubic centimetres of an 80 per cent. solution of alcohol.[4]   Stir with a glass rod.   Decant the liquid

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[1] H. Precht, *Zeit. anal. Chem.*, **18**, 514, 1879.   P. Rohland (*Zeit. anorg. Chem.*, **15**, 412, 1897: **16**, 306, 1898) does not recommend evaporation to dryness, since the dehydrated sodium chloroplatinate is less soluble in alcohol than the crystalline salt.   G. Ulex (*Zeit. anal. Chem.*, **17**, 175, 1878) recommends adding 1 to 5 c.c. of a 20 per cent. solution of glycerol to prevent the sodium chloroplatinate becoming too dry, since otherwise it might not be dissolved.   R. Fresenius, *Anleitung zur quantitativen chemischen Analyse*, Braunschweig, **2**, 290, 1905; Eng. edit., **2**, 220, 1900; G. Meillère, *Ann. Chim. anal.*, **18**, 183, 1913.

[2] The final result is independent of the kind of dish (platinum or porcelain) used in the evaporation, the presence of a little free hydrochloric or sulphuric acid and the temperature of the water bath (A. L. Winton, *Journ. Amer. Chem. Soc.*, **17**, 453, 1895).   Cases are on record where an insoluble platinous compound is formed by a reaction between the platinum of the dish and the salt.   W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **700**, 210, 1919.

[3] For the procedure when contamination with ammonium salts occurs, see E. V. Shannon, *Amer. Mineral.*, **12**, 411, 1927.

[4] A. Mitscherlich (*Journ. prakt. Chem.*, (1), **83**, 460, 1861) recommends adding the alcohol after the platinum salt, as indicated in the text.   H. Strebinger and H. Holzer (*Zeit. anal. Chem.*, **90**, 81, 1932) find that, if the alcohol contains traces of aldehyde, the precipitate does not correspond in composition exactly to K_2PtCl_6.   Apparently the platinum is in part reduced to the platinous state and as such passes into solution, leaving insoluble potassium chloride behind.

through a dry (130°), weighed Gooch crucible. Treat the mass again with 80 per cent. alcohol and decant. Repeat the decantations with 80 per cent. alcohol until the alcohol running through the crucible is colourless and the precipitate appears golden yellow, not orange yellow. Transfer the precipitate to the Gooch crucible [1] by the aid of a "policeman." Wash with 80 per cent. alcohol by half filling the crucible about six times.

Drying the Precipitate.—Drain off the alcohol,[2] and dry the precipitate at 130° to a constant weight in an air bath whose temperature is maintained constant by means of a thermostat, A, fig. 78; or in an amyl alcohol bath, fig. 58. B represents the thermometer. The copper flange CC on the front and sides of the bath is to deflect the products of combustion from the flame up the back of the bath, away from the door. Cool the crucible in a desiccator, and weigh. The increase in weight represents the potassium chloroplatinate.[3]

Calculation.—Multiply the weight of the potassium chloroplatinate by 0·3067 to get the corresponding amount of potassium chloride, and by 0·1937 to get the corresponding amount of potassium oxide. Subtract the amount of potassium chloride from the weight of the mixed chlorides in order to get the amount of sodium chloride in the given sample, and multiply the result by 0·5302 to get the corresponding amount of sodium oxide. The following are the weighings obtained with half a gram of clay from which 0·0227 grm. of the mixed chlorides was obtained :—

Dish and mixed chlorides	26·2867 grms.
Empty dish	26·2640 grms.
Mixed chlorides	0·0227 grm.
Gooch crucible and potassium chloroplatinate .	27·6898 grms.
Gooch crucible alone	27·6351 grms.
Potassium chloroplatinate	0·0547 grm.

Since $0·0547 \times 0·3067 = 0·0168$ grm. of potassium chloride,

Mixed chlorides	0·0227 grm.
Potassium chloride	0·0168 grm.
Sodium chloride	0·0059 grm.

Hence—

Weight of potassium chloroplatinate	$\times 0·1937 = 0·0106$ grm. K_2O.
Weight of sodium chloride . .	$\times 0·5302 = 0·0031$ grm. Na_2O.

If the amount of ammonium chloride and calcium carbonate used in Smith's process for the mixed chlorides contained a grm. of K_2O, and b grm. of Na_2O, a must be subtracted from the potash, and b from the soda. A blank determination showed that the materials used in the above determination contained no potassium oxide ($a = 0$), but did contain ($b =$) 0·00022 grm. of Na_2O. Hence the amount of sodium oxide is 0·0031 less 0·0002 = 0·0029 grm. per half gram of

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[1] The results are generally too high with tared filter-papers—F. H. van Leent, *Zeit. anal. Chem.*, 40, 569, 1901; R. Caspari, *Zeit. angew. Chem.*, 6, 68, 1893; F. Bolm, *Zeit. anal. Chem.*, 38, 348, 1899; C. R. Fresenius, *Anleitung zur quantitativen chemischen Analyse*, Braunschweig, 2, 290, 1905; Eng. edit., 2, 221, 1900; H. J. F. de Vries, *Chem. Weekblad*, 4, 231, 455, 1907; 5, 176, 1908.

[2] C. G. Eggertz and L. F. Nilson (*Königl. Land. Akad. Hand. Tids.*, 35, 326, 1898) here recommend drenching the precipitate with ether.

[3] According to H. Fresenius and P. H. M. P. Brinton (*Zeit. anal. Chem.*, 50, 21, 1911), if the weighed potassium chloroplatinate be caked into lumps, and not pulverulent, it should be redissolved in boiling water and evaporated in a platinum dish on a water bath in which the water is not quite boiling, again dried at 130° and weighed. The reason will appear from page 229.

the clay.   The clay in question thus contained the equivalent of 2·12 per cent. of K_2O, and 0·58 per cent. Na_2O.

Errors.—Some idea of the magnitude of the accidental errors in the determination of the potash by this and Smith's process can be obtained from the following eight independent determinations made on one sample:—

0·0106; 0·0103; 0·0108; 0·0101; 0·0109; 0·0108; 0·0104; 0·0103

The mean is 0·0105 grm. per 0·5 grm. of clay, that is, 2·10 per cent.   The deviations range approximately between ±0·04 grm. per 100 grms. of clay.   It is necessary to mention that if the clay or silicate contained sulphur, and sulphur be not removed as indicated on page 219, some sodium sulphate is almost certain to contaminate the potassium chloroplatinate.   In fact, the sulphates must be converted into chlorides by treatment with barium chloride before applying the "platinum" process.   Care must be taken that there is no excess of either sulphate or barium chloride, or the results will be high.[1]

§ 109. The Preparation of Hydrochloroplatinic Acid from Platinum Residues and Scraps.

Although usually called platinum chloride—$PtCl_4$—the reagent used for separating potassium in the form of potassium chloroplatinate is really hydro-chloroplatinic acid—H_2PtCl_6.   In order to keep down expenses, it is very necessary to collect all platinum residues, alcoholic washings and platinum scraps, in bottles provided for the purpose, and then to recover the platinum at convenient intervals.   The recovered platinum is usually converted into hydro-chloroplatinic acid.[2]

1. *Alcoholic Washings.*—Distil off the alcohol [3] and take up the residue with water; [4] add the potassium chloroplatinate residues to the solution.   Pour the

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[1] H. J. Holgen, *Chem. Weekblad*, **14**, 578, 1917; B. Turkus, *Ann. Chim. anal.*, **22**, 104, 1917; B. Schulze, *Landw. Versuchs. Stat.*, **88**, 397, 1916; T. D. Jarrell, *Journ. Assoc. Off. Agric. Chem.*, **3**, 107, 1917; B. Blount, *Analyst*, **43**, 117, 1918.

[2] L. Opificus, *Zeit. anal. Chem.*, **23**, 207, 1884; H. Precht, *ib.*, **18**, 509, 1879; G. Krause, *ib.*, **14**, 184, 1875; W. Dittmar and J. M'Arthur, *Trans. Roy. Soc. Edin.*, **33**, ii, 561, 1887; H. C. Weber, *Journ. Amer. Chem. Soc.*, **30**, 29, 1908; W. C. Zeise, *Pogg. Ann.*, **21**, 498, 1831; **40**, 234, 1837; E. Duvillier, *Compt. rend.*, **84**, 444, 1877; T. Knösel, *Ber.*, **6**, 1159, 1873; H. W. Wiley, *Journ. Amer. Chem. Soc.*, **19**, 258, 1897; *Chem. News*, **75**, 214, 1897; A. Berthold, *Zeit. angew. Chem.*, **14**, 621, 1901; J. B. and A. Tingle, *Journ. Soc. Chem. Ind.*, **35**, 77, 1916; P. Rudnick and R. D. Cooke, *Journ. Amer. Chem. Soc.*, **39**, 633, 1917; A. E. Smoll, *Journ. Ind. Eng. Chem.*, **11**, 466, 1919; L. D. Haigh and A. R. Hall, *Journ. Assoc. Off. Agric. Chem.*, **16**, 147, 1933.

[3] PURIFICATION OF ALCOHOL.—The alcohol may be recovered by re-distilling from quick-lime.   Put 1¼ litres of alcohol in a 2-litre Winchester, add 180 grms. freshly burnt quicklime in coarse powder.   Agitate every now and again for about 8 days.   Distil the alcohol into a large flask.   Add about 120 grms. freshly burnt quicklime per litre.   The alcohol which is distilled from this will be very nearly absolute—J. L. Smith, *Chem. News*, **30**, 234, 1874. The alcohol may then be mixed with powdered potassium permanganate until it is distinctly coloured; allow to stand some days until the permanganate is decomposed, and manganese oxide is deposited.   Add a little quicklime, and distil slowly.   When 10 c.c. of the distillate gives no perceptible yellow coloration when boiled with 1 c.c. of a concentrated solution of caustic soda or potash, the subsequent distillate is collected for use.   The alcohol so obtained is neutral, and gives no coloration on boiling with silver nitrate or caustic alkalies—E. Waller, *Journ. Amer. Chem. Soc.*, **11**, 124, 1889.   Absolute alcohol can be obtained from strong spirit by adding benzene and carefully fractionating.   A ternary mixture of alcohol, water and benzene distils over at 64·85°, the excess of benzene forms a binary mixture with the alcohol distilling at 68·25°, leaving pure alcohol in the still—S. Young, *Journ. Chem. Soc.*, **81**, 707, 1902.

[4] On evaporating the solution of hydrochloroplatinic acid to dryness in the presence of alcohol, hydrochloroplatinous acid—H_2PtCl_4—and ethylene are formed.   These react to produce ethylene platinous chloride, which dissolves in alcohol, forming an explosive powder when evaporated to dryness.   The dry powder is insoluble in acids.

solution into a 10 per cent. solution of sodium formate [1] and make distinctly alkaline with sodium carbonate. Heat the solution to boiling and the platinum separates as a heavy black powder. Wash with water, then with hydrochloric acid and then with water again. Dry. Ignite the powder in order to destroy organic compounds and weigh.

2. *Platinum Scraps.*—These may contain iridium, which is itself insoluble in aqua regia, but soluble in this menstruum when alloyed with platinum. Dissolve the platinum in aqua regia ($3HCl + HNO_3$) in a capacious flask on a water bath. When solution is complete, evaporate to a syrupy consistency in a large porcelain basin. Take the residue up with water, and gradually add sodium carbonate and sodium formate until the solution is alkaline.[2] Heat to boiling. Both platinum and iridium are precipitated as black powders. Decant off the supernatant liquid. Wash the residue with dilute hydrochloric acid to remove sodium salts and then with water to remove the acid. Dry the powder and ignite in a weighed porcelain crucible over a blast lamp, whereby the iridium becomes insoluble in aqua regia. Weigh.

Conversion of the Metal into Hydrochloroplatinic Acid.—Dissolve the grey powder at as low a temperature as possible in aqua regia, the nitric acid being added in small quantities at a time. In this way some nitrosylplatinic chloride, $Pt(NOCl)_2.Cl_4$, is formed. This must be destroyed, since it leads to low results in the determination of potassium. Evaporate the solution with water, whereby the nitrosylplatinic chloride is decomposed into hydrochloroplatinic acid with evolution of nitrogen oxides. Some of the latter still remain in solution. Hence, add more water and hydrochloric acid and again evaporate. These operations are repeated until no more nitrous fumes are evolved.[3] During these operations, some hydrochloroplatinous acid is formed—H_2PtCl_4. This is particularly objectionable, since it leads to high results when the chloroplatinic acid is used for the determination of potassium. In order to convert hydrochloroplatinous into hydrochloroplatinic acid, saturate the warm solution with chlorine gas and evaporate the solution at as low a temperature as possible to a syrupy consistency. Dissolve the yellowish-brown mass in water (cold), and if any insoluble iridium be present, filter, wash, ignite and weigh the residue. Subtract the result from the weight of metal taken. The difference gives the amount of platinum which has passed into solution. Dilute the solution until it contains the equivalent of 1 grm. of platinum (metal) per 10 c.c.

§ 110. The Determination of Sodium Oxide.

It will be observed that the soda has been determined by difference, and, in consequence, the resulting error is the joint effect of the error in the determination of the mixed chlorides and in the determination of the potash. The two errors may exactly or partially neutralise one another, or they may act both

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[1] D. J. de Jong, *Chem. Weekblad,* 10, 833, 1913.

[2] Take care that there is no loss by spurting during effervescence.

[3] W. Dittmar and J. M'Arthur (*l.c.*) doubt if it is possible to destroy all the nitrosylplatinic chloride in this manner. They recommend acting on the metal with hydrochloric acid and chlorine from a "chlorine Kipp." H. Precht (*Zeit. anal. Chem.,* 18, 509, 1879) and W. A. Noyes and H. C. P. Weber (*Journ. Amer. Chem. Soc.,* 30, 13, 1908) have also emphasised the necessity for removing nitric acid from the hydrochloroplatinous acid. J. S. Stas (*Chem. News,* 73, 5, 1896) removes the chlorine by dissolving the salt in water; raises the temperature of the solution to its boiling-point; saturates the solution with chlorine; and keeps the temperature of the solution at 100° until it ceases to smell of chlorine. For the preparation of hydrochloroplatinic acid by the action of a mixture of hydrochloric and chloric acids on platinum—$5HCl + HClO_3 = 3Cl_2 + 3H_2O$—see E. U. Zappi, *Anal. Fís. Quim. Argentina,* 3, 68, 1915.

in one direction. Hence a comparison of the actual values obtained for the soda—Na_2O—in eight determinations of one sample of clay, indicated below, is particularly interesting:—

0·0029; 0·0030; 0·0034; 0·0035; 0·0030; 0·0029; 0·0031; 0·0030

with a mean value of 0·0031 per half gram, and an error ranging between ±0·0003. The theory of errors furnishes a value for the error of ±0·00035 which is very near the value actually obtained when the soda—Na_2O—is determined by difference. The accidental errors per 100 grms. of clay do not differ much from +0·06 grm. Hence this method of finding the amount of sodium oxide in a clay is quite reliable and there is no need to determine the soda directly.[1]

The soda can be determined directly in the filtrate from the potassium chloroplatinate by evaporating the filtrate to a small volume, and reducing the platinum to metal by means of formic acid. Filter off the platinum; evaporate to dryness in a weighed dish; ignite at a dull red heat and finally weigh as sodium chloride,[2] or as sodium sulphate.[3]

Determination as Triple Acetate.—More recently, methods for the direct determination of sodium oxide have been based on the insolubility of sodium zinc uranyl acetate[4] and sodium magnesium uranyl acetate.[5] Neither method

[1] For a review of methods for determining sodium, see E. Einc.ke and J. Harms, *Zeit. anal. Chem.*, 99, 114, 1934. For the determination of sodium as sodium antimonate, see F. F. Beilstein and O. von Blaese, *Bull. Acad. Sciences St. Pétersbourg*, 33, 209, 1895; M. Richter-Quittner, *Biochem. Ztg.*, 133, 417, 1922; F. Lebermann, *ib.*, 152, 345, 1924; B. Kramer, *Journ. Biol. Chem.*, 41, 263, 1920; B. Kramer and F. J. Tisdall, *ib.*, 46, 467, 1921; R. L. Haden, *Journ. Lab. Clin. Med.*, 10, 236, 1924; O. von Dehn, *Zeit. physiol. Chem.*, 144, 178, 1925; A. R. Lewin, *Zeit. anal. Chem.*, 104, 406, 1936.

[2] Some of the lithium in the silicate will be found with the sodium chloroplatinate in the filtrate (page 232); most will be precipitated with the carbonate in removing lime and magnesia by Gooch and Eddy's process, but not by Smith's process. Most of the cæsium and rubidium, if present, will be found with the potassium, since both cæsium and rubidium chloroplatinates are even less soluble than the corresponding potassium salt.—W. Crookes, *Chem. News*, 9, 37, 205, 1864; R. Bunsen and G. Kirchhoff, *Pogg. Ann.*, 113, 337, 1861; *Zeit. anal. Chem.*, 1, 62, 1862; R. Bunsen, *ib.*, 2, 161, 1863. For the separation of the three chloroplatinates, see O. D. Allen, *Amer. J. Science*, (2), 34, 367, 1862; *Zeit. anal. Chem.*, 2, 68, 1863; *Chem. News*, 6, 265, 1862; R. C. Wells and R. E. Stevens, *Ind. Eng. Chem. Anal. Ed.*, 6, 439, 1934. F. Stolba's process (*Zeit. anal. Chem.*, 12, 440, 1873) with stannous chloride is not good; while F. Godeffroy's process (*Ber.*, 7, 375, 1876) with antimony chloride is very fair (A. Cossa, *Accad. Lincei*, (3), 2, 117, 1878; *Gazz. Chim. Ital.*, 8, 235, 1878). H. C. Wells, *Amer. J. Science*, (3), 43, 17, 1892; (3), 46, 186, 1893; H. H. Johnson and O. D. Allen, *ib.*, (2), 35, 94, 1863. For a review of methods for the separation of potassium, rubidium and cæsium, see W. J. O'Leary and J. Papish, *Ind. Eng. Chem. Anal. Ed.*, 6, 107, 1934. Cæsium can be determined by the perchlorate process—E. Murmann, *Oesterr. Chem. Ztg.*, 26, 164, 1923.

[3] A. Mitscherlich, *Zeit. anal. Chem.*, 1, 59, 1862; G. Werther, *Journ. prakt. Chem.*, (1), 91, 321, 1864.

[4] I. M. Kolthoff, *Pharm. Weekb.*, 60, 1251, 1923; E. Crepaz, *Ann. Chim. applicata*, 16, 219, 1926; I. M. Kolthoff, *Zeit. anal. Chem.*, 70, 304, 397, 1927; H. H. Barber and I. M. Kolthoff, *Journ. Amer. Chem. Soc.*, 50, 1625, 1928; H. Ritter, *Sprechsaal*, 63, 506, 1930; A. M. Butler and E. Tuthill, *Journ. Biol. Chem.*, 93, 171, 1931; G. W. B. Van der Lingen, *Analyst*, 57, 376, 1932; S. Z. Makarov and V. V. Bukina, *Journ. Gen. Chem.* (U.S.S.R.), 3, 881, 1933; L. Butler, *Journ. Assoc. Off. Agric. Chem.*, 17, 275, 1934; C. C. Miller and F. Traves, *Journ. Chem. Soc.*, 1390, 1936. Phosphates, if present, are removed first by adding powdered zinc carbonate—O. R. Overman and O. F. Garrett, *Ind. Eng. Chem. Anal. Ed.*, 9, 72, 1937.

[5] A. Streng, *Zeit. anal. Chem.*, 23, 185, 1884; *Zeit. wiss. Mikroskop.*, 3, 129, 1886; S. S. Miholić, *Bull. Acad. Sci. Zagrab*, 16, 1920; A. Blanchetière, *Bull. Soc. chim.*, 33, 807, 1923; A. Kling and A. Lassieur, *Chim. et Ind.*, 12, 1012, 1924; D. I. Perietzeanu, *Bul. Soc. chim. România*, 9, 17, 1927; H. Weiland, *Mitt. Kali. Forsch.-Anst.*, 21, 1927; E. R. Caley and C. W. Foulk, *Journ. Amer. Chem. Soc.*, 51, 1664, 1929; E. R. Caley, *Ind. Eng. Chem. Anal. Ed.*, 1, 191, 1929; E. R. Caley and D. V. Sickman, *Journ. Amer. Chem. Soc.*, 52, 4247, 1930; E. R. Caley, *ib.*, 54, 432, 1932; *Ind. Eng. Chem. Anal. Ed.*, 4, 340, 1932; E. R. Caley, C. T.

has as yet fully established itself as a standard process, but the results are promising. Caley and Foulk give the following details for the separation as the triple magnesium acetate:—

Dissolve the mixed chlorides in 5 c.c. of water, or less if practicable, and rapidly add the requisite quantity[1] of the reagent.[2] Keep the mixture at 19° to 20° and stir vigorously for 30 to 45 minutes—attention to these two details is essential. Immediately filter through a dry (105°), weighed Gooch crucible and wash with three successive quantities of 5 c.c. of 95 per cent. alcohol, which has previously been saturated with the triple acetate. Dry at 105° for 30 minutes and weigh. The precipitate has the composition—

$$Mg(CH_3COO)_2 . Na(CH_3COO) . 3[UO_2(CH_3COO)_2] . 6.5H_2O,$$
and contains 2·06 per cent. Na_2O.

Under the above conditions, the method gives a good separation from potassium provided not more than 0·25 grm. is present and not less than 100 c.c. of the reagent is used, but the separation from lithium is not satisfactory. The alkaline earths and ammonium are said to have no disturbing influence, but Miller and Traves find that in the presence of large amounts of calcium a double precipitation is necessary. Either the zinc or the magnesium triple acetate can be determined by volumetric or colorimetric processes.[3]

Brown and H. P. Price, *ib.*, 6, 202, 1934; G. B. van Kampen and L. Westenberg, *Chem. Weekb.*, 29, 385, 1932; T. Noda, *Journ. Soc. Chem. Ind. Japan*, 36, 635, 1933; A. Rauch, *Zeit. anal. Chem.*, 98, 385, 1934; I. I. Nazarov and L. P. Banina, *Zavodskaya Lab.*, 3, 226, 1934; M. Ishibashi and H. Kishi, *Journ. Chem. Soc. Japan*, 56, 357, 1935; F. Kögler, *Angew Chem.*, 48, 561, 1935; E. Kahane, *Journ. Pharm. Chim.*, (8), 11, 425, 1930; *Bull. Soc. chim.*, (4), 47, 382, 1930; A. Krassilchik, *Compt. rend.*, 203, 78, 1936; J. C. Canessa, *Rev. Facultad Cienc. Quim.*, 10, 87, 1935; K. M. Popov, *Kalii (U.S.S.R.)*, No. 5, 39, 1936.

[1] For 25 mgrms. or less of mixed chlorides, 100 c.c. of reagent should be used; for larger quantities the number of c.c. of reagent should be four times the number of mgrms. of mixed chlorides.

[2] MAGNESIUM URANYL ACETATE REAGENT.—Solution (A): crystallised uranyl acetate, 85 grms.; glacial acetic acid, 60 grms.; distilled water to 1000 c.c. Solution (B): crystallised magnesium acetate, 500 grms.; glacial acetic acid, 60 grms.; distilled water to 1000 c.c. Both solutions are separately heated to about 70° until the salts have dissolved. They are then mixed, cooled to 20°, kept at this temperature for a few hours and finally filtered through a dry paper into a dry bottle. The solution keeps indefinitely if stored away from direct sunlight. For the recovery of the reagent from residues, see L. Westenberg, *Verslag. Landb. Onderzoek*, No. 42E, 358, 1936.
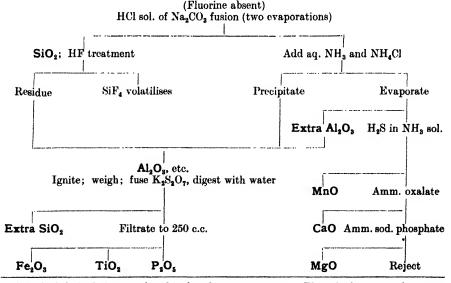
[3] A. Nau, *Bull. Soc. pharm. Bordeaux*, 65, 67, 1927; E. R. Caley, *Journ. Amer. Chem. Soc.*, 52, 1349, 1930; J. T. Dobbins and R. M. Byrd, *ib.*, 53, 3288, 1931; E. R. Caley and C. W. Foulk, *ib.*, 51, 1664, 1929; N. H. Furman, E. R. Caley and I. C. Schoonover, *ib.*, 54, 1344, 1932; I. M. Kolthoff and J. J. Lingane, *ib.*, 55, 1874, 1933; R. A. McChance and H. L. Shipp, *Biochem. Journ.*, 25, 449, 1931; A. Blenkinsop, *Journ. Agric. Sci.*, 20, 511, 1930; C. S. Piper, *ib.*, 22, 676, 1932; E. Kahane, *Bull. Soc. chim.*, (4), 47, 382, 1930; R. W. Bridges and M. F. Lee, *Ind. Eng. Chem. Anal. Ed.*, 4, 264, 1932; I. Rusznyák and E. Hatz, *Zeit. anal. Chem.*, 90, 186, 1932; R. Lang and G. Mück, *ib.*, 93, 100, 1933; S. Nagami and T. Tashiro, *Journ. Chem. Soc. Japan*, 53, 1141, 1932; F. Alten and H. Weiland, *Zeit. Pflanzenernähr. Düngung. Bodenk*, 31A, 252, 1933; *Mitt. Kali Forsch.-Anstalt*, 75, 11, 1933; *Chem. Zentr.*, (2), 2860, 1933; O. M. Smith and H. Blair, *Proc. Oklahoma Acad. Sci.*, 13, 33, 1934; K. L. Malyarov and T. Yudenich, *Zavodskaya Lab.*, 3, 904, 1934; A. Elias, *Anales Asoc. Quim. Argentina*, 23, 1, 1935; F. Alten, H. Weiland and E. Hille, *Zeit. Pflanzenernähr. Düngung. Bodenk*, 32A, 129, 1933; W. R. Wiggins and C. E. Wood, *Journ. Inst. Petrol. Tech.*, 21, 105, 1935; G. Chen, *Journ. Lab. Clin. Med.*, 21, 1198, 1936.

CHAPTER XVIII.

ABBREVIATED ANALYSES AND ANALYTICAL ERRORS.

§ 111. Exhaustive *v.* Works Analyses.

IT will now be well to review our results. The hydrochloric acid solution of the sodium carbonate fusion was evaporated twice, with an intervening filtration, and the silica filtered off, ignited, weighed and treated with hydrofluoric acid. The filtrate was precipitated twice with ammonia and ammonium chloride. The precipitate was ignited with the residue from the silica and weighed as a mixture of aluminium, ferric, titanic and phosphoric oxides. This was fused with potassium pyrosulphate, any insoluble silica filtered off, and the solution made up to 250 c.c. Of this 25 c.c. were used for the determination of iron colorimetrically and 50 c.c. for the titanic oxide.[1] The filtrate from the alumina was evaporated down to a small bulk and the last traces of alumina separated in the usual way.[2] The filtrate was treated with ammonium oxalate. The precipitated calcium oxalate was filtered off and the filtrate was treated with ammonium sodium phosphate, when a precipitate of magnesium ammonium phosphate was obtained. The next filtrate was rejected. The alkalies were determined on a separate sample. Summarised (solids to left, solutions to right):—

<div style="text-align:center">

(Fluorine absent)
HCl sol. of Na_2CO_3 fusion (two evaporations)

</div>

SiO_2; HF treatment   Add aq. NH_3 and NH_4Cl

Residue SiF_4 volatilises   Precipitate   Evaporate

Extra Al_2O_3 H_2S in NH_3 sol.

Al_2O_3, etc.
Ignite; weigh; fuse $K_2S_2O_7$, digest with water

MnO   Amm. oxalate

Extra SiO_2 Filtrate to 250 c.c.   CaO   Amm. sod. phosphate

Fe_2O_3 TiO_2 P_2O_5 MgO   Reject

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[1] And, if desired, 100 c.c. for the phosphorus (page 672). There is, however, the possibility of loss of phosphorus pentoxide by volatilisation during the ignition of the mixed oxides.

[2] The solution can then be treated with ammonia and hydrogen sulphide to precipitate the manganese sulphide (*q.v.*).

It is important in devising analytical schemes to keep the object of the analysis clearly in view.   If extreme accuracy be desired for research and other purposes, no precautions must be neglected which will ensure exact results. The analysis may have to be criticised while the analyst is in the witness box in a court of law.   In such cases he must be prepared to furnish clear, concise, complete and conclusive proofs of the accuracy of his statements.   The purity of the reagents should have been established by blank or other tests, and the degree of accuracy of the analytical process should be known.   Analyses for reports on, for instance, new clays usually call for more exhaustive details than are needed for general practice.

If the analysis is to be made for industrial work, accuracy *and* speed are of prime importance.   Such precautions must be adopted as will ensure the required degree of accuracy.   Ultra-refined processes waste time.   *Super-fluitas*, said F. Bacon, *impedit multum et reddit opus abominabile.*   A scheme of analysis might serve a given purpose admirably and yet appear grotesque if applied with another object in view.   The determination of the 0·03 per cent. of lithia usually present in Cornish stone, for instance, would be useless for ordinary technical requirements.   We should not know how to apply the information if we had it.   A certain amount of care is imperative in applying the principle, "near enough for our purpose," because unsuspected sources of faults may easily be overlooked.

The prime object of chemical analysis in industrial practice is to prevent errors of commercial importance.   These errors may arise from (1) a variation in the composition of the raw materials; (2) a wrong proportioning of these materials, *e.g.* the clays in a body mixture; (3) the need for checking the efficiency of processes of purification and grinding at different stages in the manufacture; (4) the introduction of deleterious impurities with the raw materials; (5) payment for raw materials invoiced, possibly, higher than their market value.
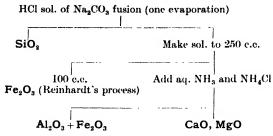
§ 112. Abbreviated Schemes of Analysis.

In purchasing raw materials, the analysis must frequently be conducted in a much shorter time than is possible by the scheme indicated in the preceding pages.   The necessary time is not available and an exact analysis may be no more useful than a close approximation.   The material may have been sold before the analyst has completed his work; the analysis, when completed, is accordingly useless for his own firm—a rival has bought the material.

The methods of analysis taught in the schools are not those which have developed under the stress of competitive practice.   The analytical chemist must therefore exercise his analytical faculties, not only in manipulative skill, but also in distinguishing between necessary precautions and unnecessary exercises in chemical gymnastics.   The two faculties are not always located in the same man.   The one is mere mechanical dexterity; the other is the quality which makes a man valuable.

Simplified Scheme of Analysis.—A simpler scheme suitable for certain analyses in routine work may be used for many purposes.   This will be understood from the representation on page 240 (solids to left, solutions to right).

For simply checking the correctness of a "mixing," the determination of the silica may suffice.   In some cases a mere determination of the loss on ignition of the dried (110)° sample will show whether it is necessary to proceed further with the analysis.   The idea is to pick out one or two components which admit of easy determination—lead and lime, for instance, in a glaze.   If these be quite normal, it is sometimes sound reasoning to infer that the different constituents have been properly proportioned.

HCl sol. of Na₂CO₃ fusion (one evaporation)

SiO₂   Make sol. to 250 c.c.

100 c.c.   Add aq. NH₃ and NH₄Cl
Fe₂O₃ (Reinhardt's process)

Al₂O₃ + Fe₂O₃   CaO, MgO

Rapid Clay Analyses.—It is possible to determine the silica, alumina and ferric oxide in a clay without using a platinum crucible and in a comparatively short time, by the following process [1]:—

Mix 0·5 grm. of the clay with six times its weight of "peroxide fusion mixture" [2] in a 30 c.c. nickel crucible with a nickel spatula. Fuse the mass for about 5 minutes at a dull red heat.[3] Cool. Place the crucible in an evaporating basin 12 cm. diameter, or in a covered beaker. Add water slowly. The action may be somewhat vigorous and care must be taken to avoid loss by spurting. The heat generated during the action will lead to a rapid dissolution of the cake. Remove the crucible and rinse it well, both inside and out. Add an excess of hydrochloric acid. Evaporate the solution to dryness. Grind the residue to powder. Dehydrate the mass at about 110° for an hour. Digest the mass with hydrochloric acid, dilute, filter, wash and ignite the residue in a porcelain crucible for total silica. Make the filtrate up to 250 c.c.

Precipitate the aluminium and ferric hydroxides in 100 c.c. of the solution by adding an excess of ammonia and ammonium chloride in the usual manner, and weigh as mixed Al₂O₃ + Fe₂O₃. Determine the ferric oxide in another 100 c.c. by, say, Reinhardt's process. All this involves 3 or 4 hours' work, excluding the 2 to 4 hours required for the silica evaporation.[4] Hence two such partial analyses can be made in a day.

§ 113. The Indirect Determination of Lime and Magnesia.

The lime and magnesia can be determined much more quickly by the indirect process than by precipitation respectively as oxalate and as ammonium magnesium phosphate.

Schaffgotsch [5] showed that calcium and magnesium carbonates separate

[1] See E. P. Fleming, *Western Chem. Met.*, **5**, 396, 1909; J. H. Walton, *Journ. Amer. Chem. Soc.*, **29**, 481, 1907; W. P. Eckdahl, *Chemist-Analyst*, **45**, 5, 1925; W. J. Rees, *Journ. Soc. Glass Tech.*, **11**, 172, 1927; C. Pertusi and E. di Nola, *Ann. Chim. applicata*, **21**, 482, 1931. Compare A. Lobanov and V. Zhitenov, *Zavodskaya Lab.*, **4**, 1277, 1935; R. I. Boroditzkaya, *Trans. Cer. Research Inst.* (*U.S.S.R.*), **46**, 1, 1935. See E. Ladd, page 510. For the rapid analysis of glass, see E. C. Sullivan and W. C. Taylor, *Journ. Ind. Eng. Chem.*, **6**, 897, 1914; W. Pape, *Sprechsaal*, **60**, 163, 1927; S. S. Zhukovskaya and S. T. Balyuk, *Zavodskaya Lab.*, **3**, 485, 1934; M. B. Vilensky, *Journ. Amer. Cer. Soc.*, **19**, 91, 1936.

[2] PEROXIDE FUSION MIXTURE.—Mix 4 parts by weight of the purest sodium peroxide with 1 part of the purest sodium hydroxide. Sodium peroxide usually contains traces of silica. The amount can be determined by a blank experiment and an allowance made for the 3 grms. of peroxide fusion mixture used.

[3] For a still more rapid method of decomposition, see page 265.

[4] For systems of accelerated evaporation, see H. J. S. Sand, *Journ. Soc. Chem. Ind.*, **26**, 1225, 1907; W. Hempel, *Ber.*, **21**, 900, 1888; C. Jones, *Journ. Anal. App. Chem.*, **3**, 121, 1889; R. Fessenden, *Chem. News*, **61**, 4, 1890; E. Donath, *Chem. Ztg.*, **32**, 1107, 1908; T. Brugnatelli, *Gazz. Chim. Ital.*, **8**, 16, 1878; J. W. Gunning, *Zeit. anal. Chem.*, **26**, 725, 1887; A. Gawalovski, *ib.*, **12**, 181, 1873; C. Zengelis, *ib.*, **45**, 758, 1906.

[5] F. C. Schaffgotsch, *Pogg. Ann.*, **104**, 482, 1858; **106**, 294, 1859; A. K. Christomanos, *Zeit. anal. Chem.*, **42**, 606, 1903; J. Knoblock, *ib.*, **37**, 733, 1898; O. Brill, *Zeit. anorg. Chem.*, **45**, 275, 1905. See page 220.

from a solution containing a great excess of ammonium carbonate and ammonia probably in the form of double ammonium carbonates. A certain amount of magnesium carbonate is, however, hydrolysed under these conditions, and the precipitation of the magnesia is not therefore quite complete. Gooch and Eddy [1] have shown that the separation is completed in a relatively short time if the solution contains an excess of alcohol.

Determination of the Mixed Oxides.—After the sodium carbonate fusion and removal of the silica and alumina in the usual manner, the filtrate from the alumina is boiled down to a small volume,[2] and an equal volume of alcohol and 50 c.c. of Gooch and Eddy's solution (page 220) are added. In about half an hour the precipitate is filtered off and washed with the same solution and dissolved in a small volume of dilute hydrochloric acid. The solution is then neutralised with ammonia, and an equal volume of Gooch and Eddy's solution and alcohol added. The precipitate is washed as before, ignited in a weighed platinum crucible and weighed as a mixture of $CaO + MgO$.[3]

Transformation of the Mixed Oxides to Sulphates.—Add, very carefully, sufficient dilute sulphuric acid [4] to combine with all the lime and magnesia in the crucible. Evaporate the solution to dryness, then gradually raise the temperature of the crucible to the full heat of a Bunsen burner [5] for about a quarter of an hour. Weigh [6] the contents of the crucible as mixed $CaSO_4 + MgSO_4$.

Calculations.—Suppose that W represents the weight of the mixed oxides, w the weight of the mixed sulphates; then, if u represents the weight of the SO_3 present, $w - W = u$. By the method of page 223, therefore, we have the two equations:

$$MgSO_4 + CaSO_4 = w; \quad \text{and} \quad 0 \cdot 6651 \ MgSO_4 + 0 \cdot 5882 \ CaSO_4 = u$$

Hence,

$$CaSO_4 = 8 \cdot 649w - 13 \cdot 004u; \quad MgSO_4 = w - CaSO_4$$

In illustration, suppose the mixed oxides weighed 0·0265 grm., and the mixed sulphates 0·0703 grm., it follows that the mixture contains 0·0385 grm. of $CaSO_4$ and 0·0318 grm. of $MgSO_4$. But

$$CaSO_4 \times 0 \cdot 412 = CaO; \quad \text{and} \quad MgSO_4 \times 0 \cdot 335 = MgO$$

Hence the given mixture has 0·0159 grm. CaO and 0·0107 grm. MgO.[7]

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[1] F. A. Gooch and E. A. Eddy, *Amer. J. Science*, (4), **25**, 444, 1908; *Chem. News*, **97**, 280, 1908; J. M. Stillman and A. J. Cox, *Journ. Amer. Chem. Soc.*, **25**, 732, 1903; E. Dreschel, *Journ. prakt. Chem.*, (2), **16**, 169, 1878; O. Foote, *Gazz. Chim. Ital.*, **24**, i, 207, 1894. According to O. Bertrand (*Monit. Scient.*, (3), **10**, 477, 1880), at 10°, 1 part of calcium carbonate is soluble in 13,980 parts of water containing ammonium chloride; in 8380 parts of water containing ammonium sulphate; and in 14,438 parts of water containing ammonium nitrate.

[2] If any alumina separates, it must be of course filtered off.

[3] If baryta and strontia be present, they will be included with these bases. To evaluate the mixture by a titration process, see A. Trabert, *Compt. rend.*, **119**, 1009, 1894; *Chem. News*, **71**, 26, 1895.

[4] The addition of sulphuric acid is not a very safe operation for an analytical process. It is best to add an ammoniacal solution of ammonium sulphate containing a little ammonium chloride—W. L. Scott, *Chem. News*, **1**, 144, 1860.

[5] If no fumes of sulphuric acid come from the crucible on ignition insufficient sulphuric acid was probably added. In that case, more sulphuric acid must be added when the crucible has cooled. A large excess of sulphuric acid should be avoided. For the determination of the alkaline earths as crystalline sulphates, see J. D. M. Smith, *Journ. Soc. Chem. Ind.*, **44**, 40 T, 1925.

[6] The mixture is a little hygroscopic, and must not be needlessly exposed to the air before weighing.

[7] P. J. Fox (*Journ. Ind. Eng. Chem.*, **5**, 910, 1913) and C. J. Schollenberger (*Chemist-Analyst*, **16**, 6, 1927) precipitate the calcium as oxalate and magnesium as ammonium arsenate

§ 114. Permitted Errors.

If all the constituents in any given silicate have been determined, the numbers, in the ideal case, should add up to 100 per cent. The proximity of the actual sum to the ideal 100 is a valuable check on the accuracy of the work. Absolute identity would not represent perfect work.[1] The errors due to incomplete washing; dust; inevitable impurities in the best of reagents; action of the reagents and solutions on the glass and porcelain, all tend to make the total greater than 100. On the other hand, mechanical losses through imperfect cleaning of the vessels in transferring liquids and solids from one vessel to another; accidental spilling of drops; the slight solubility of the precipitates, all tend to reduce the total below 100 per cent. There is but a remote probability—perhaps less than one in a hundred—that the two sets of errors will exactly balance one another, and the ideal 100 be obtained. The coincidence would be mere chance, and when it does occur it is somewhat embarrassing. It is necessary to decide on limiting deviations above and below 100 for satisfactory work. If these limits be exceeded, the analysis is to be condemned. Hillebrand[2] places these limits at 99·75 and 100·5; Washington[3] prefers 99·5 and 100·75. If the total falls below 99·5, there is strong presumptive evidence that some constituent has been either overlooked or ignored. In the analysis of clays for technical purposes no pretence is made to exhaust the possible constituents. Only those constituents of technical importance are determined. Hence, it is advisable to extend the lower limit. In reports on clays and related materials we make ±0·5 the permitted limiting deviations from 100. If the total falls below 99·5, it is advisable to find the missing constituent. If the analysis pretends to be exhaustive, the lower limit should be raised.

The practice of adjusting the results of an analysis to an exact 100 is utterly bad—although it rather appeals to a business man who is ignorant of what is implied, and likes to see the data "properly balanced," as he calls it. Apart altogether from the ethics of the computation, and the temptation to "cook" a defective analysis, the trimming of an analysis to a round 100, as Fresenius[4] has pointed out, "prevents others from judging the accuracy of the results," and, in consequence, makes chemists reasonably sceptical as to the value of the work. The figures must always be given as they are obtained, and it is just here that the integrity of the analyst meets its first test.[5] There is an impression that a satisfactory summation is a sufficient criterion of accurate work. As a matter of fact, *a satisfactory summation is no proof that*

(page 282) in the same solution. The mixed precipitate is filtered and washed and dissolved in dilute sulphuric acid. The oxalate is determined by permanganate titration and, in the same solution, potassium iodide is added and the liberated iodine titrated with thiosulphate (page 285).

[1] F. Jordis, *Zeit. anorg. Chem.*, **45**, 362, 1905. If the weighings be not all reduced to "weight *in vacuo*," it is easy to prove that the sum of the several constituents with ordinary analytical weights, and with *perfect* work, cannot add up to 100.

[2] W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **700**, 30, 1919.

[3] H. S. Washington, *Manual of the Chemical Analysis of Rocks*, New York, 24, 1904. For the limits of accuracy in the analysis of alloys, see E. A. Lewis, *Metal Ind.*, **2**, 304, 1910; *Journ. Soc. Chem. Ind.*, **31**, 96, 1912. See also J. Grossmann, *ib.*, **18**, 977, 1899. Of 3391 silicate analyses in the *Bull. U.S. Geol. Sur.* (**14**, 1903; **28**, 1904) the sum of 1253 varied from 99 to 99·99 per cent., and 1846 from 100 to 100·99 per cent.—H. H. Robinson, *Amer. Journ. Sci.*, (4), **41**, 257, 1916.

[4] R. Fresenius, *Quantitative Chemical Analysis*, London, **2**, 101, 1900.

[5] Clay analyses have been published where the sum total of constituents makes over 104 per cent., and that not a misprint. We can only admire the honesty of the analyst—a professional by the way. The work should have been repeated. Its publication was ill-advised.

the separations have been correctly performed. This is well demonstrated by the variation in the ratio $SiO_2 : Al_2O_3$ in different analyses of the same clay by different men.[1]

Another meretricious system of reporting commercial analyses may be illustrated by quoting the last three lines of an analysis of ball clay from a "clay expert's" report:—

Alkalies	1·83
Undetermined constituents	0·18
Total	100·00

The "undetermined constituents" will not deceive a chemist who has grasped the significance of the errors incidental to all methods of analysis, but it may mislead [2] those who have not devoted special attention to the subject.

Dittrich [3] has analysed artificial mixtures containing known quantities of the principal constituents which occur in silicate rocks and found the limits of error [4] to be as follows:—

Table XXXVIII.—Accidental and Constant Errors in Silicate Analyses.

Constituent.	Limits (per cent.).
Alumina	0·15 and −0·25
Ferric oxide	+ 0·2 and −0·3
Lime	− 0·1
Magnesia	−0·1
Potash (Bunsen's process) . .	+ 0·1
Potash (Smith's process) . .	−0·1 and −0·2
Soda (Bunsen's process) . .	+ 0·2 and −0·3
Soda (Smith's process) . .	− 0·1 and −0·2

Each limit will naturally vary with the skill of the analyst, with the process of analysis and be dependent upon the number of separations involved in the analysis.   In general, *the greater the number of separations, the greater the errors of the analysis.*

In order to find what accidental errors might be expected in clay analyses,

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[1] Naturally, something is then wrong.   If baryta were overlooked in a glaze analysis, the "total" might be satisfactory, and yet the alumina, tin, etc., might be high, especially if sulphates be present.

[2] "100 per cent. analyses" are frequently "crocks."   As a matter of fact, there was a discrepancy between the above result and the vitreous qualities of the clay.   Another analyst reported 3·0 per cent. potash (K_2O), and 1·8 per cent. soda (Na_2O).   This corresponds with 4·8 per cent. alkalies, and agreed with the known properties of the clay.   For "alkalies," see page 214.

[3] M. Dittrich, *Neues Jahrb. Min.*, 2, 69, 1903.

[4] By "accidental error" is understood the irregular deviations from the arithmetical mean which are just as likely to have a positive as a negative value.   A "constant error" is an error due to well-defined causes which make the error incline more in one direction than in another —*e.g.* errors due to a defect in the pipette, burette or measuring flask, solubility of precipitate, etc.   The correction tables, pages 22 and 40, are intended to neutralise constant errors due to the causes named.   For a discussion on accidental and constant errors, see J. W. Mellor, *Higher Mathematics for Students of Chemistry and Physics*, London, 510, 537, 1926.   The accuracy of the results can be expressed in several different ways, *e.g.*: "the results are within, say, 0·1 of each other"; "the results are accurate to ±0·1 per 100 parts of the sample"; "the results are accurate to ±0·1 per 100 parts of the given constituent in the sample"; etc.

eight independent analyses of one homogeneous sample of clay were made in a laboratory by an analyst accustomed to work with the processes recommended in this book. Details have been indicated in the preceding text. The results are here collected in Table XXXIX.

Table XXXIX.—Accidental Errors in Eight Analyses of a Clay.

Constituent.	Mean values per cent.	Maximum and minimum deviations.
Silica . . .	60·47	⊣ 0·07
Titanic oxide . .	1·20	± 0·07
Alumina . . .	21·90	± 0·10
Ferric oxide . .	1·50	± 0·06
Lime . . .	1·45	± 0·08
Magnesia . .	1·10	⊣ 0·08
Potash . .	2·11	⊣ 0·04
Soda . . .	0·62	⊥ 0·04
Loss on ignition .	9·30	∴ 0·05

The above numbers take no account of constant errors. Dittrich's Table XXXVIII indicates both constant and accidental errors. The errors would be different if different amounts of each constituent were present and different methods of analysis used. *The relative error involved in separating a relatively small amount of a constituent is greater than in separating a large quantity,* because, in the former case, a small quantity of impurity and the slight solvent action of the mother liquid have a greater influence on the final result. The sulphur and chlorine (Table XXXIX) have not been determined; without these and certain other constituents, the total is 99·65 per cent. This series of analyses, with some hundreds of other analyses, has led us to place the check for commercial analyses at 100±0·5, as indicated above.

It will be obvious that if each constituent had its maximum deviation, or if each constituent had its minimum deviation, the total might fall outside the assigned limit and the analysis be condemned although the error with no constituent exceeded the tolerated limits. The chance of this event happening is over 1 in 100,000,000 analyses. The magnitude of the errors might be reduced by working in a clearer atmosphere than sometimes prevails in the testing laboratory of a works and using platinum utensils throughout. The numbers given above represent analyses made under routine conditions by the method described in what precedes.

The Committee of the American Chemical Society "On Uniformity in Technical Analysis"[1] reported the results of 35 analyses of one sample of an argillaceous limestone made by different laboratories. These are somewhat startling in their want of agreement. We have given the mean of two concordant analyses by the two referees in the second column of the table and the maxima and minima results sent to the committee by the different analysts in the last two columns.

[1] *Journ. Amer. Chem. Soc.*, **26**, 1652, 1904; **28**, 223, 1906. See also "Report of the Subcommittee on the Uniformity in Analysis of Materials for the Portland Cement Industry," *Journ. Soc. Chem. Ind.*, **21**, 12, 1223, 1902; H. W. Stanger, *ib.*, **21**, 1216, 1902; W. F. Hillebrand, *Journ. Franklin Inst.*, **155**, 109, 181, 1903; G. Tschermak, *Centr. Min.*, 1, 1916. Compare G. E. F. Lundell, *Ind. Eng. Chem. Anal. Ed.*, **5**, 221, 1933.

Table XL.—Comparative Analyses of an Argillaceous Limestone.

Constituent.	Standard.	Minimum.	Maximum.
Silica . . .	18·14	16·58	18·92
Titanic oxide .	0·22	0·11	0·82
Alumina .	5·70	4·42	7·35
Ferric oxide .	1·71	1·06	2·83
Manganese oxide .	0·04	none	1·70
Lime . . .	37·65	35·26	41·98
Magnesia .	1·93	0·92	3·05
Potash . .	1·14	0·46	2·68
Soda . . .	0·33	0·11	2·00
Loss on ignition .	32·27	31·94	32·88
Phosphoric oxide .	0·18	0·12	0·65
Sulphur . .	0·27	none	0·71
Sulphur trioxide .	0·012	none	0·69
Carbon . .	0·64	0·41	2·03
Carbon dioxide .	30·68	28·65	31·65

§ 115. The Chief Sources of Error in Analyses.

Every careless step in an analysis shows itself in material mistakes. The student must reason closely to keep his solutions correct. He cannot go on long with mere enthusiasm and boasting. His own results bring him the greatest reproaches. His experiments silently humble him, and he is laughed at by the forces which he cannot avenge.—W. CROOKES.[1]

It may be here instructive to follow Jüptner's plan and summarise the more important sources of error.[2] Most of these have already been discussed in detail.

(1) *Imperfections in sampling.*—This, as already indicated, is a prolific source of discrepancies in analytical results.

(2) *Errors due to mistakes and lack of skill, e.g.* mixing the samples; arithmetical errors in calculations; faulty reading of burettes, weights, tables; sticking of Erdmann's float; dirty vessels. The susceptibility of a worker to errors of this kind is greater in badly equipped laboratories, imperfect illumination, over-work, with consequent fatigue and lapses of attention, and with a laboratory near a source of dust. Experiments with clays favour the development of dust and clay dust settling in beakers and funnels conduces to high results.

(3) *Impure reagents, e.g.* phosphates in ammonium nitrate used for washing the alumina and the ammonium phosphomolybdate precipitates; iron and carbon in the zinc used for reducing ferric salts for the permanganate titration; fluorine in the hydrogen peroxide used for the titanium determinations; silica in the sodium carbonate flux; alkalies in the calcium carbonate used in Smith's process; vanadium in the potash; chlorides or sulphates in the sodium carbonate or nitrate.

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[1] *Chem. News,* **19**, 1, 1869; "Care in Laboratory Work," G. Surr, *Min. Eng. World,* **39**, 780, 1913; G. Tschermak, *Centr. Min.,* 1, 1916.

[2] H. von Jüptner, *Journ. I. S. Inst.,* **49**, 80, 1896; *Chem. News,* **74**, 81, 1896; C. B. Dudley, *Journ. Amer. Chem. Soc.,* **15**, 501, 1893; A. B. Prescot, *Chem. News,* **53**, 78, 88, 1886; S. H. Collins, *Univ. Durham Phil. Soc.,* 1, 1909; E. A. Lewis, *Journ. Soc. Chem. Ind.,* **31**, 96, 1912; V. Zotier, *Bull. Sci. pharmacol.,* **24**, 298, 1917.

(4) *Faulty measuring apparatus, e.g.* the weights may be in error; the volumetric apparatus may not be consistent; the volumetric measurements may not be corrected for variations of temperature.[1]

(5) *Errors in manipulation, e.g.* action of water on the glass vessels; introduction of sulphur from rubber stoppers used in sulphur determinations; moisture in the apparatus used in fluorine determinations; losses by spitting when an alkaline carbonate is neutralised by an acid.

(6) *Errors due to faults in the process of analysis.*—Examples occur during the precipitation of barium sulphate (page 691); incomplete oxidation of carbon in the wet combustion process (page 616); solubility of silica (page 167); adsorption of salts by precipitates—*e.g.*, the "alumina" precipitate and by the calcium carbonate in the Smith's process for alkalies; the solvent action of hydrochloric acid on sulphides—*e.g.* lead sulphide.

(7) *Personal errors, e.g.* defects in the perception of colour in colorimetric processes; methods of reading burette; method of adding reagents to solutions (page 157); etc. The result is that one chemist gets consistently better results with one process than with another, whereas the converse may be true for another chemist.[2] The differences of opinion as to the relative merits of the cyanide, iodine and electrolytic processes for copper might be cited in illustration. By studying the properties of precipitates, the number of filtrations and of transfers from vessel to vessel, common sense will sometimes decide in favour of one of a number of rival processes. Other things being equal, *the "margin of safety" is greater, that is, the risk of error is less, the fewer the separations involved in isolating a given constituent.* The more complex the method of separation, the greater the influence of the personal factor. Other things being equal, *that method of analysis is safest which depends least on the skill of the operator.* In order to reduce the personal factor to a minimum in the determination of phosphorus and manganese in iron and steel, where accuracy *and* speed are of vital importance, and where the *general* composition and range of variation of the substances to be analysed are known, methods have been devised, chiefly by C. H. and N. D. Ridsdale,[3] for the rapid determination of the constituents just mentioned. These methods—styled *mechanicalised processes* and *analoid processes*—are followed "mechanically" with prescribed quantities of solvents, measured reagents and ready-made tablets of solid reagents introduced at definite assigned temperatures. In this way the trouble, expense and uncertainty involved when differences occur in analyses made by different chemists are reduced to a minimum.

Proposals to *standardise processes of analysis* crop up from time to time. It is suggested that the methods of analysis in which manufacture and sale depend upon the results shall be standardised by an authoritative committee [4] and

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[1] H. Lundén, *Svensk. Kem. Tids.*, **24**, 96, 1912.

[2] This explains some puzzling statements which confront the analyst who "consults the originals." Given three processes A, B and C for a particular determination, the author of the process A may quote analyses to prove that A is superior to B and C; the author of B may try to prove that his process is superior to A or C; and similarly, the author of process C may set out to prove that C is superior to A and B.

[3] C. H. and N. D. Ridsdale, *Journ. I. S. Inst.*, **1**, 332, 1911; *Analyst*, **50**, 425, 500, 1925; *Journ. Soc. Chem. Ind.*, **38**, 15T, 1919; C. H. Ridsdale, *ib.*, **38**, 200R, 1919; C. O. Bannister, *ib.*, **39**, 351R, 1920; *Journ. Proc. Inst. Chem.*, 169, 1920; W. H. Herdsmann, *Journ. West Scot. I. S. Inst.*, 4, 1912; C. T. Nesbitt, *Chem. World*, **3**, 295, 1914; *Met. Chem. Eng.*, **12**, 793, 1914.

[4] For discussions on the standardisation of analytical processes, see *Journ. Soc. Chem. Ind.*, **3**, 2, 210, 345, 356, 1884; J. Pattinson, *ib.*, **3**, 17, 1884; R. R. Tatlock, *ib.*, **3**, 307, 1884; J. C. Bell, *ib.*, **2**, 109, 1883; A. R. Ling, *ib.*, **22**, 677, 1903; C. Richardson, *ib.*, **20**, 334, 1901; J. White, *ib.*, **24**, 390, 1905; H. D. Richmond, *ib.*, **22**, 676, 1903; G. Lunge, *Chem. News*, **47**, 210, 1883; B. Blount, *ib.*, **86**, 177, 1902; H. von Jüptner, *ib.*, **74**, 81, 1896; *Journ. I. S. Inst.*, **49**, 80, 1896; W. D. Richardson, *Journ. Ind. Eng. Chem.*, **2**, 99, 1910. Page 244.

periodically revised. In this way, a greater uniformity in results might be expected. Progress would not necessarily be arrested, because improved methods would be examined by the committee periodically and the less satisfactory methods cancelled.

(8) *Errors due to calculations based on different atomic weights.*—In this work we assume that the table of international atomic weights is used. It may seem heresy to inquire if this is the best we can do. It will be obvious that the atomic weight question is of the greatest importance. It is not uncommon to find a difference of a few per cent. between the maximum and minimum values for the atomic weights found by different or by the same experimenters. The maximum value for the reliable determinations of the atomic weight of magnesium given by Clarke is 24·706; the minimum value 24·016.[1] In calculating the ratio $MgO: Mg_2P_2O_7$, page 212, we assumed the atomic weight of magnesium to be 24·32. It seems that under the ordinary conditions of chemical analysis, the weight may deviate at least (possibly more than) $\pm 0·3$ from this value. This means that instead of taking the factor 0·3621 for converting a given weight of magnesium pyrophosphate into magnesia, we require a factor somewhere between 0·3643 and 0·3604. With small amounts of magnesia, it does not matter which be used—0·36 will do quite well. With larger amounts of magnesia, the result may be affected by over one-fourth per cent. It might therefore be personally interesting for an analyst to find if he works under the 0·3643 or the 0·3604 conditions.

Many chemists recommend the use of an old discarded value for the atomic weight of platinum—197—in potash determinations for calculating the amount of KCl or K_2O equivalent to the K_2PtCl_6 precipitate.[2] There can be little doubt that the best chemists, working with the best available instruments, under the best conditions, with the purest available materials and with a few selected reactions, get a number nearer 195 than 197. Why then recommend 197? If, by a given analytical process, 197 gives a result nearer the correct value than 195, it is obvious that the former number should be used in that process. It is, indeed, possible that if the atomic weight had been determined by the same reaction as used in the analytical process, a number different from 195 would have been obtained. Again, the difference in the results obtained between "amount taken" and "amount found" in the determination of antimony by the sulphide and iodine titration processes, respectively, suggests that the atomic weight of antimony is nearer 120 than 121·76, because the results by the titration process are always about one per cent. lower than with the gravimetric sulphide process,[3] though the former is known to be the more accurate method.

§ 116. The Statement of the Results.

It would be an advantage if different analysts adopted one uniform practice in stating their results, since analyses would then be much easier to read. The Fifth International Congress of Applied Chemistry at Berlin agreed that—

1. The name of the constituent is to be followed by the formula;
2. By the name of an acid, the acid itself and neither its anhydride nor its ion is to be understood; and

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[1] F. W. Clarke, *A Recalculation of the Atomic Weights*, Washington, 222, 1910.
[2] F. Wolfbauer, *Chem. Ztg.*, **14**, 1246, 1890.
[3] E. G. Beckett, *Beitrag zur Bestimmung des Antimons*, Zürich, 59, 1909; L. A. Youtz, *Zeit. anorg. Chem.*, **37**, 337, 1903; A. Kolb and B. Formhals, *ib.*, **58**, 189, 1908; O. Collenberg and G. Bakke, *Tids. Kemi Bergvesen*, **18**, 1097, 1924.

3. When the results are calculated in the form of metal oxide and acid anhydride, the latter is to be written either as "sulphuric anhydride, SO_3," or as "sulphuric acid (calculated as anhydride) SO_3."[1]

Washington and Hillebrand[2] recommend stating the results somewhat in the following order: SiO_2, Al_2O_3, Fe_2O_3, FeO, MgO, CaO, Na_2O, K_2O, H_2O (ignition), H_2O (below 110°), CO_2, TiO_2 ZrO_2, P_2O_5, SO_3, Cl, F, S, (FeS$_2$), Cr_2O_3, V_2O_3, MnO, NiO, CoO, CuO, ZnO, BaO, SrO, Li_2O, C, NH_3, and organic matter. The idea is to keep the important oxides at the head of the list, so that the general character of the silicate can be seen at a glance. This is no doubt excellent. For clays, we prefer to keep the titanium among the important constituents since, in the higher grades of clay, it is often as important a constituent as iron and more important than magnesia. The P_2O_5, SO_3, Cl, F, CO_2 and carbon are best kept as a separate group. For glazes and frits, we also prefer to keep certain bases in a separate group. The following lists represent the order we use for commercial analyses of clays and glazes and similar materials, where the purpose of the analyses is different from that of Washington and Hillebrand:—

CLAY DRIED AT 109° C.	GLAZE DRIED AT 100° C.
Hygroscopic moisture lost at 109° C.	Hygroscopic moisture lost at 100° C.
Silica (SiO_2).	Silica (SiO_2).
Titanic oxide (TiO_2).	Alumina (Al_2O_3) and Ferric oxide (Fe_2O_3).[3]
Alumina (Al_2O_3).	Lime (CaO).
Ferric oxide (Fe_2O_3).	Magnesia (MgO).
Manganese oxide (MnO).	Potash (K_2O).
Magnesia (MgO).	Soda (Na_2O).
Lime (CaO).	Loss when calcined over 100° C.[4]
Potash (K_2O).	
Soda (Na_2O).	
Loss when calcined over 109° C.	Lead oxide (PbO).
	Tin oxide (SnO_2).
	Zinc oxide (ZnO).
Chlorine (Cl).	Barium oxide (BaO).
Fluorine (F).	
Phosphoric oxide (P_2O_5).	Fluorine (F).
Sulphur (S).	Phosphoric oxide (P_2O_5).
Sulphur trioxide (SO_3).	Sulphur trioxide (SO_3).
Carbon (C).	Carbon dioxide (CO_2).
Carbon dioxide (CO_2).	Boric oxide (B_2O_3).

If there is any evidence showing the way the acids and bases are combined, the amounts may be stated separately—e.g. calcium carbonate (whiting), white lead, calcium fluoride. When the way the acids and bases are combined is open to doubt, it is best to leave the adjustment to those who intend to transform the analysis of, say, a glaze into a recipe.[5]

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[1] W. Fresenius, *Zeit. anal. Chem.*, **44**, 32, 1905. See also *Chem. News*, **53**, 186, 1886; E. C. C. Stanford, **16**, 29, 190, 1874; C. G. Hopkins, *Journ. Amer. Chem. Soc.*, **29**, 1312, 1907.

[2] H. S. Washington, *Amer. J. Science*, (4), **10**, 59, 1900; *Prof. Paper U.S. Geol. Sur.*, **14**, 24, 1903; **28**, 7, 1904; W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **700**, 31, 1919.

[3] There is usually no need to separate the constituents of the ammonia precipitate unless phosphates be present.

[4] The interpretation of "loss on ignition" is somewhat indefinite with glazes, and is rather a qualitative indication of the character of the glaze in question.

[5] For an example of the discrepancies which may arise when the analyst attempts to go beyond his facts, and show the mode in which the "bases" and "acids" are combined, compare H. M. Noad, *Journ. Chem. Soc.*, **14**, 43, 1862; and A. Voelcker, *ib.*, **14**, 46, 1862; *Chem. News*, **3**, 77, 285, 315, 1861. See also R. Haines, "The Analysis of Mineral Waters and the Arrangement of the Results," *Chem. News*, **4**, 29, 1861; W. West, *Pharm. Times*, **1**, 44, 1847; C. Palmer, "The Geochemical Interpretation of Water Analyses," *Bull. U.S. Geol.*

It is sometimes difficult to decide how best to report the separate constituents in an analysis, since curious practices prevail in buying and selling which are not always those most convenient for the consumer. Manganese ores, for instance, may be sold on their per cent. of metallic manganese, or manganese peroxide; cerium is weighed as cerium dioxide, but the earths are sold on their per cent. Ce_2O_3; chromium ores are valued on their Cr_2O_3 contents; tungsten ores on their WO_3 contents; tantalum and vanadium ores on the amount of the respective elements equivalent to Ta_2O_5 and V_2O_5 they contain; while uranium ores are valued on their equivalent U_3O_8.[1] Analysts must then bow to the inexorable fetish—custom.

Sur., **479**, 5, 1911; R. B. Dole, "The Hypothetical Combinations in Water Analysis," *Journ. Ind. Eng. Chem.*, **6**, 710, 1914; W. T. Schaller and R. C. Wells, *Journ. Wash. Acad. Sci.*, **3**, 47, 416, 1913; C. E. van Orstrand and F. E. Wright, *ib.*, **4**, 514, 1914; M. Roloff, *Zeit. öffent. Chem.*, **14**, 53, 1908; G. S. Rogers, *Econ. Geol.*, **12**, 56, 1917.

[1] G. T. Holloway, *Trans. Inst. Min. Met.*, **21**, 569, 1912.

CHAPTER XIX.

ELECTRO-ANALYSIS.

§ 117. Some Definitions.

IF two platinum plates be dipped in an aqueous solution of, say, copper sulphate, and the plates be connected by wire with the poles of a battery or accumulator, metallic copper will be precipitated on one plate, and if the conditions be suitable, practically all the copper will separate in the form of a compact coherent metallic film. If the plate with the film of copper be washed, dried and weighed, the increase in the weight of the plate will represent the amount of copper which was present in the solution under investigation.

The process of decomposition is called *electrolysis*; the solution undergoing decomposition is called an *electrolyte*; the two plates by which the current enters and leaves the electrolyte are called *electrodes*. The electrode by which the current is conventionally supposed to enter the electrolyte is called the *anode*; and the other electrode is called the *cathode*.[1]

What has just been stated about the solution of copper sulphate applies to many other metallic salts. When such solutions are electrolysed, the metal is deposited on the cathode. But with solutions of lead and manganese salts, the peroxides are sometimes deposited on the anode. In applying these facts to practical analysis, it is convenient to make the dish holding the electrolyte the electrode, generally the cathode, on which the deposit is to be collected.

The quantity of electricity which passes through the solution in unit time, or the speed of the current, is measured by an *ammeter*. The unit is called an *ampere*.[2] The unit of the electric pressure [3] driving the electric current along the circuit is called the *volt*,[4] and the voltage of the current is measured by the *voltmeter*. The current is regulated by coils of wire or incandescent lamps, which obstruct the flow of the current of electricity and fritter the

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[1] It is always easy to determine which wire from the battery or accumulator belongs to the cathode, and which to the anode, by wetting a piece of blotting-paper with an aqueous solution of potassium iodide and starch, and allowing the tips of the two wires to touch the wet paper about a quarter of an inch apart. The paper in the vicinity of the wire to be attached to the anode will be coloured blue. If the blotting-paper be soaked in a solution of sodium chloride and phenolphthalein, the paper in the vicinity of the cathode will be coloured red. Paper prepared in this way is called "pole paper," and is sold in booklets or rolls like litmus paper.

[2] The ampere "is represented by the unvarying electric current which, when passed through a solution of silver nitrate in water, deposits metallic silver at the rate of 0·001118 grm. per second."

[3] Also called the electromotive force, or potential.

[4] The volt "is represented by the electrical pressure that if steadily applied to a conductor whose resistance is one ohm will produce a current of one ampere."

energy of the electric current down into heat. The unit of resistance is called the *ohm*.[1]

There is an interesting relation—*Ohm's law*—between these magnitudes:

$$\text{Quantity of electricity (amps.)} = \frac{\text{Pressure (volts)}}{\text{Resistance (ohms)}}$$

Consequently, decreasing the resistance opposed to, or increasing the voltage of, a current will increase the quantity passing through a circuit per second (amperage); and, conversely, increasing the resistance or decreasing the voltage will decrease the quantity of electricity passing through the circuit per second.

§ 118. Some Factors which determine Success in Electro-Analysis.

1. *Pressure of the Current—Decomposition Voltage.*—For the decomposition of every metallic solution, the pressure of the electric current must exceed a certain minimum value. This minimum voltage is characteristic of the particular solution under investigation. For instance

Sulphates.	volts.	Chlorides.	volts.
Nickel sulphate	2·09	Nickel chloride	1·85
Cadmium sulphate	2·03	Cadmium chloride	1·88
Cobalt sulphate	1·92	Cobalt chloride	1·78

A current of many amperes might be passed through a solution of cobalt sulphate without any visible decomposition; only when the voltage exceeds 1·92 volts will cobalt be deposited. If a solution contains a mixture of salts of different metals, the electrodes appear as if they exerted a kind of selective action which really depends upon the minimum voltages required to effect the decomposition of the different metallic salts. This peculiarity of the salts can be used to effect the separation of the different metals. In a solution containing cadmium and cobalt sulphates, for example, cobalt will be deposited with a voltage less than 2·02 volts, and greater than 1·92 volts. When all the cobalt is deposited, increasing the voltage above 2·03 volts will lead to the deposition of cadmium.

2. *Strength of the Current—Current Density.*—The weight of a given metal deposited by a current of electricity is proportional to the quantity of electricity (coulombs) passing through the solution; and the weights of different metals deposited by the same quantity of electricity (coulombs) are directly proportional to the chemical equivalents of the metals in the solutions (Faraday's laws). Thus, a given quantity of electricity will deposit the relative quantities of the different metals indicated in the last line of the following scheme:—

	Al	Ni	Co	Sn(ic)	Cu	Cd
Atomic weight	26·97	58·69	58·94	118·70	63·57	112·41
Chemical equivalent	8·99	29·345	29·47	29·675	31·785	56·205

The quantity of metal deposited in a given time, that is, the rate of deposition, is dependent upon the strength of the current in amperes. The deposited metal redissolves in the electrolyte and, consequently, the rate at which the metal is deposited must exceed the rate at which it redissolves. The metal is only deposited from the solution in the immediate vicinity of the cathode. Hence, other things being equal, the greater the area of the cathode the more

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[1] The ohm is the unit of resistance and "is represented by the resistance offered to an unvarying electric current by a column of mercury, at the temperature of melting ice, 14·4521 grms. in mass, of a constant sectional area and a length of 106·3 cm."

metal available for deposition, and, *mutatis mutandis,* the greater the rate at which the metal is redissolved. Hence the strength of current necessary to deposit the metal will depend upon the area of the cathode.

The amount of current per unit area (per second) is called the *current density*—100 sq. cm., that is, 1 sq. decimetre, is generally taken as unit area. Hence "a current density of 2 amperes" means that 2 amperes should be used for each 100 sq. cm. of cathode area.

While the tendency of a metal to redissolve in the solution fixes a lower limit to the strength of current which may be used for electro-analysis, the tendency of the metal to form spongy, non-adherent films when deposited too rapidly prevents the use of currents exceeding a certain maximum strength (amperage per unit area of cathode).

It is highly important, for accurate work, to precipitate the metal in a coherent film which is easily washed and weighed. The condition of the deposited metal is not only dependent upon the voltage and the current density, but is also determined by such factors as the nature of the solution from which the metal is deposited, the amount of free acid and the temperature. These "optimum" conditions can only be determined by trial and failure.

3. *Nature and Concentration of Electrolytes.*—Enough salt should be present in the solution to carry the current, otherwise hydrogen or some other element may cause the film of metal to become spongy and impure. The more concentrated the solution, the greater the amount of metal in solution in the neighbourhood of the cathode. The nature of the salt undergoing decomposition is of importance. Copper nitrate, for example, gives better results than copper sulphate; and nickel sulphate is far more satisfactory than nickel nitrate. Better deposits are frequently obtained with complex salts like the metallo-cyanides and double oxalates, than with the simple sulphates or nitrates.

4. *Nature and Concentration of Foreign Salts in the Electrolyte.*—A current density which gives a perfectly pure coherent deposit of, say, copper when no other metal is present may give a very impure deposit when, say, arsenic is present, particularly if the decomposition voltage of the foreign salt be near that of the copper salt. The greater the concentration of the foreign salt, the greater the danger of its simultaneous deposition with the copper.

5. *Temperature.*—The time needed for the complete electrolysis of certain solutions, *e.g.* copper or nickel sulphate, lead nitrate, is frequently shortened by working at a higher temperature, but the deposits are not always so good as those formed at lower temperatures. When working at higher temperatures, if the solution be heated to its boiling-point, there is a danger that the deposit may be loosened from the cathode, and an accurate determination is then impracticable. Hence, normally, the solution under electrolysis is not boiled.

6. *Condition of the Electrolyte.*—Only those metallic salts in the vicinity of the electrodes can be decomposed by the current and the diffusion of more salt from the body of the solution to the vicinity of the electrodes is comparatively slow. Hence adequate stirring of the solution will greatly accelerate the speed of precipitation by supplying fresh metal faster than it can be supplied by simple diffusion to take the place of the metal withdrawn from the solution. When artificial means are used to agitate the solution during electrolysis, a greater maximum current density can be used. One of the electrodes is usually rotated, and the consequence is that the current may be considerably increased without injuring the deposit; and deposits which require several hours under ordinary conditions may be completed in as many minutes. This subject will be discussed later.

In giving directions for electrolytic separations, or in stating the results of experiments, the following factors, apart from those connected with the apparatus, are thus to be considered:—

1. Pressure of electric current in volts.
2. Current density in amperes per square decimetre.
3. Nature and concentration of the electrolyte.
4. Nature and concentration of foreign salts dissolved in the electrolyte.
5. Temperature of the electrolyte.
6. Condition of the electrolyte—at rest or stirred.

If attention be paid to these details, many electrolytic methods of analysis rival in accuracy, neatness and rapidity the best of the gravimetric and volumetric processes available for the same metal. In consequence, a number of electrolytic methods have won a permanent place in analytical chemistry. True enough, the time required for the electrolysis may be prolonged, but very little attention is needed during the actual electrolysis. Indeed, many electrolyses can be safely left 12 hours—say overnight—without attention. Those methods involving the use of rotating electrodes enable a determination to be made in 10 or 15 minutes. An example is given on page 347.

§ 119. The Apparatus for Electro-Analysis.

When a relatively small number of determinations is made, the outfit will be different from that used for routine work. The former will alone be considered here. For the latter, special text-books [1] must be consulted. The determination of copper is conveniently taken as a standard process for reference. This is also particularly appropriate not only because of the typical character of the process, but also because the Mansfield Oberberg und Hüttendirection, in 1867, offered a prize for a rapid and accurate method for the determination of copper in ores. The prize was won by C. Luckow [2] for an electrolytic process. This gave an impetus to electro-analysis generally.

A plan of the outfit for occasional work is shown in fig. 79. The current from an accumulator B passes through the variable resistance R to the decom-
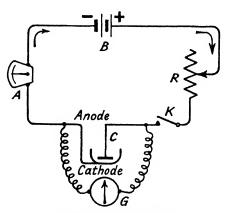
FIG. 79.—Plan of Fig. 80.

position cell C, then through the ammeter A, and back to the accumulator. A voltmeter G is placed in metallic contact with the cathode and anode. Usually

[1] A. Classen, *Quantitative Analyse durch Elektrolyse*, Berlin, 1908; B. B. Boltwood's trans., New York, 1908; A. Fischer, *Elektroanalytische Schnellmethoden*, Stuttgart, 1908; F. M. Perkin, *Practical Methods of Electro-chemistry*, London, 1905; J. Riban, *Traité d'Analyse Chimique Quantitative par Électrolyse*, Paris, 1899; B. Hollard and L. Bertiaux, *Analyse des Métaux par Électrolyse*, Paris, 1909; E. F. Smith, *Electro-analysis*, Philadelphia, 1918; B. Neumann, *Theorie und Praxis der analytischen Elektrolyse der Metalle*, Halle a. S., 1897; J. B. C. Kershaw's trans., London, 1898.

[2] C. Luckow, *Zeit. anal. Chem.*, 8, 23, 1869; 19, 1, 1880.

a couple of 2-volt E.P.S. accumulator cells (*B*) will suffice for the current.[1] The key *K* is for making or breaking the circuit as desired.

A photograph of the apparatus is shown in fig. 80. The electrolytic cell shown at *C* is the type recommended by Classen. It consists of a platinum
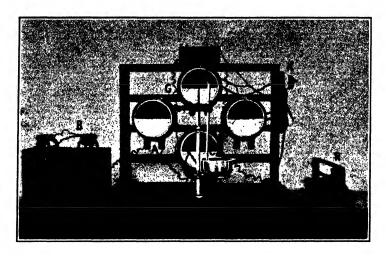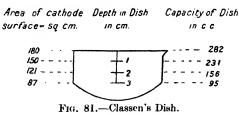
FIG. 80.—The Apparatus for an Electro-analysis (Stationary Electrodes).

basin, about 250 c.c., with or without an inner matte surface.[2] This serves as the electrode for collecting the deposit. A perforated platinum disc fixed to a stout platinum wire may be used for the other electrode.[3] The dish rests on a brass 'retort ring' to which three platinum points have been fixed to ensure

FIG. 81.—Classen's Dish.

electrical contact between the retort ring and the platinum dish. The ring is clamped to a glass rod fixed to a heavy iron base. The platinum wire supporting the disc is also fixed by a suitable clamp to the same glass rod. The glass rod serves to insulate the disc from the dish. If otherwise, the current would

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[1] For the use and adjustment of a D.C. (direct current) lighting circuit, see E. B. Kauffman, *Met. Chem. Eng.*, 13, 534, 1915.

[2] The nature of the surface of the electrodes is of importance. Some metals give less satisfactory deposits on hammered surfaces than on spun and polished surfaces. In the determination of lead as peroxide, the precipitate only adheres firmly to the electrode when the surface has been roughened by means of, say, a sand-blast. A woven platinum gauze electrode—flag electrode—is also recommended in special cases. The electrode must be quite clean or a poor deposit will be obtained.

[3] Several other types of anode and cathode are in use—dishes, cones, cylinders, gauzes, spiral wires. The important points about the electrodes are: (1) they must not be attacked by the electrolyte nor absorb gas; (2) they must be of such a shape that the density of the current on the electrode which receives the deposit is as homogeneous as possible; and (3) the shape must favour rapid diffusion of the electrolyte from one electrode to the other.

short circuit and not pass through the decomposition cell. Binding screws are fixed to the clamps, so that the dish and disc can be put into electrical contact with the battery.[1]

Classen's dish, shown in fig. 81, is 9 cm. in diameter and 4·2 cm. deep. It holds about 250 c.c., and weighs between 35 and 37 grms. The dish shown in the diagram held 231 c.c., when filled to within 1 cm. of the upper edge, and 156 c.c. when filled to within 2 cm. of the upper edge. With a disc anode, the best distribution of the current is obtained by adjusting the disc so that it is exactly in the centre of the dish and about 2 or 3 cm. below the upper edge.

If the electrolytic cell is to be heated, a thin asbestos board or silica plate is placed under the dish, and the vessel is heated by a small burner (fig. 80) so as to ensure a uniform temperature.

The resistance or rheostat R, shown in the photograph, is made from platinoid wire wound on an asbestos-covered brass tube, or on a slate frame. By moving the sliding contact along a bar, any desired resistance can be obtained within the capacity of the instrument.[2]

The ammeter A is an instrument with a small internal resistance—so small that it can, for most purposes, be neglected. In consequence, the ammeter is kept in the main circuit all the time an experiment is in progress. A 20-amp. meter reading to $\frac{1}{10}$ amp. will suffice for the work described in this book.[3]

The voltmeter G has a relatively large internal resistance, and if placed in the main circuit would afford so much resistance to the passage of the current that very little current would pass at all, or the coils of the voltmeter would be burnt out. If, for instance, the voltmeter has a resistance of 1000 ohms and the electrolytic cell 2 ohms, the ratio of the current passing through the decomposition cell to that passing through the voltmeter will be as $500 : 1$. The voltmeter may be left in the shunted circuit all the time an electrolysis is in progress. A voltmeter reading 0 to 20 volts graduated in half-volts is sufficient.[4]

§ 120. The Electrolytic Determination of Copper.

Copper can be satisfactorily deposited from solutions acidified with nitric or sulphuric acid, but not with hydrochloric acid except under special conditions. Nitric acid gives better results than sulphuric acid. The determination will be here described in some detail to serve as a type for later references.[5]

1. *Cleaning the Electrodes.*—The electrodes must be perfectly clean. Never touch the depositing surfaces of the electrodes with the fingers, to avoid danger of contaminating them with grease. Clean electrodes are absolutely necessary for good deposits. Silver soap or round-grained sea sand applied with a soft cloth or small sponge is commonly used for scouring and polishing. Grease is removed either by heating the electrodes to redness,[6] or by immersion in a saturated solution of chromic acid (or potassium dichromate) in concentrated

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[1] It is easy to make less expensive supports than the one here described. Much depends upon the "taste" of the worker. The construction of apparatus for electrolytic work lends itself to what Ostwald calls "Basteln"—pottering. The stand in the background of fig. 80 has ammeters and voltmeters for running two independent determinations at the same time.

[2] Numerous other types are used. Some of these will be found described in the textbooks cited above.

[3] Ammeters with a range 0–2 amps. reading in hundredths, provided with a shunt for reading 0–20 amps. in tenths, will be ample for work other than that described here.

[4] In purchasing a new instrument, one reading 0–3 volts in tenths, provided with a shunt for reading 0–30 in half-volts, will be found useful for work with rotating electrodes.

[5] W. C. Blasdale and W. Cruess, *Journ. Amer. Chem. Soc.*, **32**, 1231, 1910; D. J. Demorest *Journ. Ind. Eng. Chem.*, **5**, 216, 1913.

[6] Never heat platinum electrodes unless every particle of the previous deposit has been removed, otherwise an alloy may be formed which will spoil the apparatus. See page 98.

sulphuric acid. Wash with distilled water and dry by warming. The cathode is cooled in a desiccator and weighed.

2. *Preparation of the Electrolyte.*—Dissolve a gram of copper sulphate in 140 c.c. of distilled water; add 5 to 10 c.c. of nitric acid (sp. gr. 1·42), so as to make the solution between 8 and 10 per cent. nitric acid.[1] The solution is placed in the weighed platinum dish. If the electrolysis is to be conducted at a temperature above atmospheric, say 60°, warm the solution in the dish and adjust the burner so as to maintain the necessary temperature.

3. *Adjustment of the Apparatus.*—The apparatus is fitted up as indicated in fig. 79. See that all the metallic contacts—battery connections, connections with the voltmeter, ammeter, resistance and electrolytic stand—are clean and rigid. If otherwise, the contacts may, later on, offer so much resistance that the current is either weakened or interrupted. The anode should be adjusted in the centre of the dish, and at such a distance (0·5 to 1 cm.) from the cathode that a high voltage is unnecessary when the current has started. It is best to start with the whole of the variable resistance in the circuit. Then when the circuit is closed, the resistance is cut down until the current rises to, but does not exceed, the maximum required for the electrolysis. Cover the platinum dish with a watch-glass cut in two pieces, and provided with notches for the anode and also for a thermometer, if the electrolysis is to be conducted at a higher temperature. The watch-glass prevents loss by the spray carried off with the gases liberated at the anode.

4. *The Electrolysis.*—Complete the circuit and adjust the resistance so that when the potential difference is from 2·0 to 2·5 volts[2] the current density falls between 0·5 and 1·0 amp.[3] per 100 sq. cm.[4] A bright red film will flash over the cathode surface as soon as the circuit is closed. The electrolysis will be finished in about 4 hours.

If the electrolysis is to run overnight, a current density of about 0·1 amp. will suffice. A little more nitric acid—2 c.c.—should also be added, since some of the nitric acid is converted into ammonia by the hydrogen liberated at the cathode, and this is inclined to cause a spongy deposit.
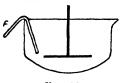
FIG. 82.

To find if all the copper has been deposited, raise the level of the solution by the addition of a little distilled water. If no copper is deposited on the newly exposed cathode surface after a run of about 15 minutes, it may be assumed that the electrolysis is finished.[5] Or, a drop of the electrolyte may be transferred to a filter-paper

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[1] If the solution contains much free nitric acid, it should be evaporated to dryness, and the residue dissolved in the prescribed amount of nitric acid and water. If the solution contains much free sulphuric acid, the solution should be neutralised with ammonia, and the necessary amount of nitric acid added.

[2] The voltage and current density depend upon the resistance of the electrolytic cell, which in turn depends upon the conductivity of the solution, the size and shape of the electrodes and their distance apart. It is frequently inconvenient to regulate these two factors to correspond exactly with prescribed directions. In that case, bring the voltage to the desired value and let the current adjust itself to the required amperage. This is particularly the case with separations where the decomposition voltage is of prime importance.

[3] If other metals are present in the solution, keep to the lower amperage.

[4] From fig. 81 we see that the dish with 150 c.c. of solution offers a cathode surface of approximately 120 sq. cm. Hence, if 0·8 amp. is needed per 100 sq. cm., a cathode surface of 120 sq. cm. will require a current of 1 amp. read on the ammeter.

[5] Classen (*l.c.*) places a small strip of bright platinum foil in contact with the cathode (*F*, fig. 82), but not touching the anode. If after half an hour no deposit is formed on the foil immersed in the liquid, it is safe to assume that the electrolysis is complete. If a deposit forms, it must subsequently be dissolved off by connecting the foil to the anode.

moistened with a few drops of potassium ferrocyanide and ammonium acetate. A brownish-red colour shows that all the copper has not been deposited and that it is necessary to continue the electrolysis. When no coloration appears on repeating the test, the electrolysis is finished.

5. *Washing and Drying the Deposited Metal.*—Since the precipitation has been made in an acid solution, some consider that the current should not be stopped until the acid liquid has been removed, otherwise the dissolution of the deposited copper will start before the plates can be washed, and thus lead
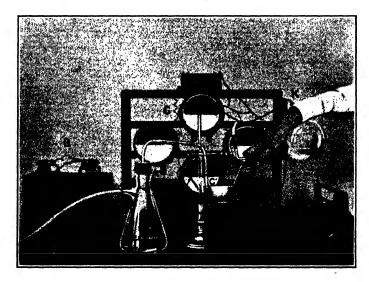
FIG. 83.—Washing the Cathode Dish.

to low results. In most cases, however, sufficiently accurate results will be obtained by breaking the current, and immediately [1] pouring the solution into an empty beaker, and rapidly rinsing out the basin with hot distilled water. Finally, wash three times with about 5 c.c. of alcohol,[2] and once with ether.[3] Dry the precipitated copper in an air bath at about 80°; cool in a desiccator and weigh.

When it is desired to wash the deposit free from acid before stopping the current, the acid liquid is syphoned off (by suction) into a filtration flask, and at the same time fresh distilled water is poured into the basin until the washings are free from acid. This is illustrated in fig. 83. The deposit is then washed, as indicated above.

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[1] F. Rüdorff (*Zeit. angew. Chem.*, 6, 5, 1892) adds 10 drops of a saturated solution of sodium acetate just before breaking the circuit. The acetic acid which is set free does not attack the copper immediately, and in consequence there is sufficient time to wash the plates before appreciable action has occurred.

[2] The alcohol should give no residue on evaporation to dryness. The alcohol should also have been distilled over lime. Instead of absolute alcohol, methylated spirit free from mineral oil can be used. The methylated spirit is purified by standing in contact with caustic soda for a few days, and distilling. Freshly burnt lime is now added to the distillate, and after standing 24 hours, the spirit is decanted into a distilling flask containing some freshly burnt lime and redistilled.

[3] The ether is supposed to have been distilled over caustic potash. Some omit the ether treatment.

6. *Errors.*—If the current density be too high, the deposit may be "burnt." In that case, the copper, instead of appearing as a bright red coherent film, is coloured more or less brown and appears more or less pulverulent and non-adherent. If the current be acting for too long a time, there is a possibility that some of the sulphuric acid may be reduced by the hydrogen liberated at the cathode to form hydrogen sulphide. In that case, some copper sulphide will be formed and this leads to the development of dark brown spots on the copper. Or with nitric acid ammonia may be formed, leading to a spongy deposit.

If arsenic or antimony be present, these elements may be deposited with the copper, giving it a dull or even a grey appearance. In that case, the copper deposit may be heated to dull redness to volatilise the oxides of arsenic and antimony.[1] Dissolve the resulting copper oxide in nitric acid and repeat the electrolysis. Hollard and Bertiaux say that the addition of a little ferric sulphate lessens the danger of precipitating arsenic and the addition of a little lead nitrate the deposition of antimony.[2] If much arsenic, antimony or bismuth[3] be present, they should be separated chemically before the electrolysis.

Silver, if present, will be deposited with the copper, and should therefore be removed from the solution before the electrolysis, or the metal deposited on the cathode can be weighed as "silver + copper." The mixed metals are then dissolved in nitric acid, and the silver determined by the addition of a little hydrochloric acid in the usual way. Tin and mercury, if present, may also be deposited with the copper.

In illustration of the results which may be obtained with the process just described:—

Copper taken	.	.	25·08	25·08	25·08	25·08 per cent.
Copper found	.	.	25·08	25·05	25·07	25·04 ,,

7. *Recording the Results.*—The results entered in the note-book will include the following data:—

1. Current pressure: 2·2–2·5 volts.
2. Current density: 0·5 amp.
3. Electrolyte: 1 grm. of copper sulphate with 8 to 10 per cent. of nitric acid, made up to 150 c.c.
4. Foreign salts: no foreign metallic salts were present.
5. Temperature: 15°–20°.
6. Electrodes: stationary.
Time, 4¼ hours.

The weighings were:—

Cathode and deposit	.	.	.	.	.	.	36·3242 grms.
Cathode	.	.	.	.	.	.	36·0734 ,,
Copper deposit	.	.	.	.	.	.	0·2508 grm.

Hence, the sample contained 25·08 per cent. metallic copper.

8. *Cleaning the Deposit from the Electrode*—In the case of copper, the deposit can be readily removed from the platinum dish by the action of dilute nitric acid and subsequent washing with distilled water.

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[1] A platinum dish will not stand this treatment for long.

[2] For the deposition of antimony with copper, see W. Hampe, *Chem. Ztg.*, 16, 417, 1892; E. F. Smith and D. L. Wallace, *Zeit. anorg. Chem.*, 4, 273, 1893; A. Hollard and L. Bertiaux, *Bull. Soc. chim.*, (3), 31, 900, 1904; H. Hölemann, *Zeit. anal. Chem.*, 81, 161, 1930.

[3] For the effect of bismuth, see A. Classen, *Quantitative Analyse durch Elektrolyse*, 80, 123, 1908; *Zeit. anorg. Chem.*, 4, 234, 1893; E. F. Smith and J. Salter, *ib.*, 3, 415, 1893; E. F. Smith, *ib.*, 5, 197, 1894; W. Hampe, *Zeit. anal. Chem.*, 13, 187, 354, 1874.

Electrolysis of Sulphuric Acid Solutions.—It may be desirable to precipitate the copper from a sulphuric acid solution free from nitric acid. The deposits of copper are not then quite so red in colour as when nitric acid is present. Between 7 and 10 per cent. H_2SO_4 is added, that is, about 4 c.c. per 100 c.c. of solution. According to C. Engels, the deposits are better if from 1 to 1·5 grms. of hydroxylamine sulphate be present.[1] About 2·5 volts and a current density of 0·5 amp. are used. The best temperature is from 70° to 80°. Between 1 and 1½ hours are needed for the electrolysis. The process is used when copper is to be separated from zinc, cadmium, nickel and less than 0·1 grm. of iron. If over this amount of iron—say, up to 0·6 grm.—be present, the electrolysis must be conducted at atmospheric temperature.[2] The time needed for the electrolysis is then between 2 and 2½ hours. For an overnight electrolysis, use rather less sulphuric acid, 0·5 grm. of hydroxylamine sulphate and a current density of about 0·1 amp.

Electrolysis of Ammoniacal Solutions.—Add ammonia to a solution of copper chloride containing less than 2 grms. of copper. When the precipitate has re-dissolved, add 20–25 c.c. of ammonia (sp. gr. 0·96) for quantities of copper up to 0·5 grm., and 30–35 c.c. for quantities up to 1 grm. Add 3–4 grms. of ammonium nitrate. If up to 0·5 grm. of copper be present, use a current density of 0·5 amp., and so proportionally up to 2 amps. for 2 grms. of copper. Time: about 2 hours. If insufficient ammonia be present, a brown non-adherent deposit collects on the anode, which falls off and contaminates the cathode deposit.[3]

Electrolysis of Nitric Acid Solutions.—According to Gilchrist and Cumming,[4] the deposition is complete, even in the presence of a large excess of nitric acid, if sufficient urea be present to destroy all the nitrous acid—

$$CO(NH_2)_2 + 2HNO_2 = 3H_2O + 2N_2 + CO_2$$

[1] A. Classen recommends urea for the same purpose. In that case, some carbon is deposited with the copper, and the subsequent correction is troublesome.

[2] O. Foerster, *Zeit. angew. Chem.*, 19, 1890, 1906.

[3] F. Oettel, *Chem. Ztg.*, 18, 47, 879, 1894; F. Rüdorff, *Ber.*, 21, 3050, 1888.

[4] E. Gilchrist and A. C. Cumming, *Trans. Faraday Soc.*, 9, 186, 1913; H. Cloukey, *Journ. Ind. Eng. Chem.*, 6, 1266, 1914.

For the electro-analysis of copper, see S. C. Schmucker, *Zeit. anorg. Chem.*, 5, 199, 1894; F. Foerster and O. Seidel, *ib.*, 14, 106, 1897; J. Siegrist, *ib.*, 26, 273, 1901; E. B. Spear, C. Chow and A. L. Chesley, *Eighth Inter. Cong. App. Chem.*, 21, 93, 1912; E. P. Schoch and D. J. Brown, *ib.*, 21, 81, 1912; J. G. Fairchild, *Met. Chem. Eng.*, 11, 380, 1913; E. P. Koepping, *ib.*, 14, 441, 1916; E. Keller, *Bull. Amer. Inst. Min. Eng.*, 2093, 1913; B. Koch, *Chem. Ztg.*, 37, 873, 1913; G. Wegelin, *ib.*, 37, 989, 1913; W. Theel, *ib.*, 39, 179, 1915; C. Lind, *ib.*, 37, 1372, 1913; *Report, Journ. Ind. Eng. Chem.*, 7, 546, 1915; M. Nakao, *Journ. Pharm. Soc. Japan*, 666, 1915; J. Guzmán and J. Sanz, *Ann. Soc. Esp. Ph. Ch.*, 13, 289, 1915; *Ann. Fis. Quim.*, 13, 289, 1915; J. Guzmán and T. Batuecas, *ib.*, 14, 38, 1916; J. Guiteras, *ib.*, 17, 209, 1919; J. Guzmán and A. Rancaño, *ib.*, 27, 269, 1929; F. G. Hawley, *Eng. Min. Journ.*, 102, 307, 1916; 110, 162, 1920; D. Nishida, *Journ. Chem. Soc. Japan*, 26, 1257, 1923; A. T. Etheridge, *Analyst*, 49, 371, 1924; J. Lukas and A. Jílek, *Chem. Listy*, 18, 378, 1924; 20, 18, 1926; W. Moldenhauer, *Zeit. angew. Chem.*, 39, 454, 1926; R. A. F. Hammond, *Journ. Inst. Metals*, 37, i, 268, 1927; E. B. Holland and G. M. Gilligan, *Ind. Eng. Chem.*, 20, 533, 1928; E. Philippi and F. Hernler, *Mikrochem. Emich Festschr.*, 241, 1930; T. L. Kelly and J. J. Molloy, *Journ. Amer. Chem. Soc.*, 53, 1337, 1931; G. Galfaian, *Zeit. anal. Chem.*, 99, 32, 1934; W. L. Miller, *Ind. Eng. Chem. Anal. Ed.*, 8, 431, 1936.

PART III.

ANALYSIS OF GLASSES, GLAZES, COLOURS AND COMPLEX SILICATES.

CHAPTER XX.

THE ANALYSIS OF GLAZES, GLASSES, ENAMELS AND COLOURS.

§ 121. The Selection of the Sample.

THE glaze to be analysed may be—partly or wholly—raw or fritted.[1] In the latter case, the method of analysis is the same as for glasses, enamels and frits. Again, if a fired glaze be in question, it is usually necessary to chip the glaze from the body with a chisel and hammer. In that case, it is impossible to prevent part of the body being analysed with the glaze, because (1) the glaze while being fired dissolves some of the constituents of the body; and (2) the mechanical separation of chippings of the glaze from the body, even under a good lens, is laborious and unsatisfactory.[2] In the case of iron enamels, the analysis will include part of the intermediate flux between the enamel and the metal.[3] To remove a glaze or enamel from a body, de Luynes[4] recommends roughening the surface of the glaze with emery or carborundum paper or a file, and coating the roughened surface with wet glue. The glue is dried and baked in an air bath. During the drying, the glue sometimes drags part of the glaze or enamel from the body. The glue can be removed by means of boiling water and the fragments washed on a filter-paper.

As a rule glazes contain silica, boric oxide, alumina, ferric oxide, lime, magnesia, lead oxide and alkalies.[5] There may also be present tin oxide, baryta, phosphoric and sulphuric oxides, and fluorine. In special cases, zirconia, antimony and arsenic may be present. In the case of colours, zinc, chromium, cobalt, nickel, manganese, copper, bismuth, cadmium, titanium, uranium, molybdenum and gold may be found. The last six elements named are rare.[6] Selenium is occasionally found in clear glasses and frits. The general scheme for the separation of the more common elements is as follows:—

I. *Hydrogen sulphide group.*
  (1) *Copper group.*—Insoluble in sodium sulphide—*e.g.* copper, lead, bismuth, cadmium.
  (2) *Arsenic group.*—Soluble in sodium sulphide—*e.g.* arsenic, antimony, tin.

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[1] An examination of the constituents removed by treatment with dilute acids and the determination of the carbon dioxide and water, will often furnish valuable data for reconstructing such glazes from the analysis.

[2] The interpretation of the analysis is then more or less obscure and vague.

[3] Fragments of iron may be removed with a magnet.

[4] V. de Luynes, *Compt. rend.*, **134**, 480, 1902.

[5] Along with carbon dioxide and combined water with raw and partially fritted glazes.

[6] Molybdenum, gold, silver, iridium, rhodium and platinum are extremely rare. Tungsten is rare, although traces are common enough in tin glazes. It is introduced as an impurity with the tin oxide, and its presence is not always objectionable.

II. *Ammonia group* or *basic acetate group*—*e.g.* aluminium, iron, titanium, chromium.

III. *Ammonium sulphide group*—*e.g.* zinc, manganese, cobalt, nickel.

The treatment when the rarer elements are present is discussed later. The boric oxide is determined on a separate sample by the methods described later. We will first discuss the metals precipitated by hydrogen sulphide in acid solutions and follow by a discussion of the processes required when zirconium, manganese, uranium, cobalt, nickel, chromium, zinc, etc., are present. In any case, the given sample is ground to a fine powder [1] (page 103).[2]

§ 122. " Opening " the Sample.

The method to be used for the analysis of a glaze is determined by the result of the qualitative analysis. The colour of the glaze is often a good indication of the colouring oxide present. If the glaze contains unfritted white or red lead, a preliminary digestion with dilute acetic, hot hydrochloric or nitric acid will remove the lead. The insoluble residue is fused [3] with sodium carbonate (as indicated page 144), and the fused mass digested with, say, dilute nitric acid. The solution may be added to that obtained by the preliminary digestion with nitric acid.

If all or part of the lead be fritted, and the frit is not completely decomposed by digestion with these acids,[4] another procedure must be followed. The frit can be fused in a platinum crucible provided an oxidising atmosphere is rigidly maintained in the interior of the crucible. If tin oxide be present, it will dissolve slowly in the molten sodium carbonate.

Fusion with Sodium Hydroxide or Peroxide.—An enamel, glaze or glass containing antimony,[5] arsenic or tin oxide can sometimes be conveniently heated with eight to ten times its weight of sodium hydroxide [6] (or sodium peroxide) in a silver or nickel crucible at a dull red heat until the mass is fused. Dissolve the fused mass, when cold, in a little water or dilute hydrochloric acid. The objection to the use of caustic alkalies is their tendency to froth over, and the

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[1] Note, finely powdered glass and similar materials are almost universally hygroscopic—E. T. Allen and E. G. Zies, *Journ. Amer. Ceram. Soc.*, **1**, 739, 1918.

[2] For general analyses of ores and minerals, see W. R. Schoeller, *Analyst*, **40**, 90, 1915; Thürmer, *Glashütte*, **61**, 833, 1931; for glasses, L. Ronnet, *Ann. Falsif.*, **11**, 26, 1918; R. Schmidt, *Sprechsaal*, **57**, 240, 1924; G. A. Kall, *ib.*, **59**, 510, 1926; W. H. Withey, *Journ. Soc. Glass Tech.*, **11**, 124, 1927; V. Dimbleby, *ib.*, **11**, 153, 1927; J. D. Cauwood, J. H. Davidson and V. Dimbleby, *ib.*, **12**, 7, 1928; W. Singleton and R. C. Chirnside, *ib.*, **12**, 18, 1928; G. E. F. Lundell and H. B. Knowles, *Journ. Amer. Ceram. Soc.*, **10**, 829, 1927; E. C. Sullivan and W. C. Taylor, *Journ. Ind. Eng. Chem.*, **6**, 897, 1914; G. E. F. Lundell, *ib.*, **25**, 853, 1933; for glass sands, Glass Standards Committee, *Journ. Soc. Glass Tech.*, **19**, 26, 1935.

[3] Care must be taken in using a platinum crucible when metallic oxides and salts are present, or the crucible may be attacked during the sodium carbonate fusion.

[4] For the joint effect of acids and a metal like zinc, see T. Moore, *Chem. News*, **67**, 267, 1893.

[5] For the volatilisation of antimony during the fusion with sodium carbonate, see H. N. Warren, *Chem. News*, **67**, 16, 1893.

[6] A "pinch" of powdered wood charcoal—quarter gram—accelerates the decomposition of tin oxides, cassiterite, etc. The solution of the cassiterite will be complete in three or four minutes, but the heating is continued a little longer in order to burn off the carbon—C. A. Burghardt, *Chem. News*, **61**, 260, 1890; *Proc. Manchester Lit. Phil. Soc.*, (4), **3**, 171, 1890; A. Gilbert, *Zeit. öffent. Chem.*, **16**, 441, 1910. This process also works well with chrome iron ore, wolframite, etc. H. T. Loram (*Proc. Chem. Soc.*, **27**, 60, 1910) recommends fusing the "tin ore" in a silver crucible, with six or seven times its weight of potassium hydroxide, and its own weight of potassium cyanide. Extract the cold mass with water. Dissolve all in dilute hydrochloric acid. Boil to expel cyanogen compounds.

time necessary for the solution of the powder.[1] The following is the best way of conducting the operation:—The crucible [2] is placed in a circular hole cut in a sheet of $\frac{1}{8}''$ asbestos millboard, so that the crucible when pressed tightly into the aperture projects on the upper side about a quarter of an inch. The lid of the crucible is tapped on an agate mortar with a round-faced hammer, so that the lid fits the crucible with its convex side downwards. Any portions projected from the melting mass on the under side of the lid travel to the centre of the lid and drop back into the crucible. A single Bunsen burner will heat a small charge to a dull red heat. This usually suffices for the decomposition. The mouth of the crucible is kept cool and the fused salt does not creep over the edges of the crucible. The results are usually excellent. A similar remark applies to the fusion with sodium peroxide as described for chromite,[3] page 527.

The heat required for the decomposition may be furnished by a reaction between the sodium peroxide and the organic matter of the substance [4] under investigation or organic matter purposely added.[5] When starch and organic matter are used the fusion does not usually proceed quietly but is attended by slight explosions which project the fused mass on the sides and lid of the crucible. Walton and Scholz [6] observed that the fusion is much quieter if zinc sulphide be substituted for the starch, and Parr [7] found that the addition of a small amount of potassium persulphate led to better fusion and more complete decomposition. Suppose a lead frit be under investigation. The operation is conducted as follows:—

A round-bottomed nickel crucible about 30 c.c. capacity and 4 cm. in diameter is charged with 8 grms. of powdered sodium peroxide; 0·5 grm. of the finely powdered (200's lawn) frit; (say) 1·2 grm. of finely powdered zinc sulphide; and 0·3 grm. of potassium persulphate.[8] Each constituent must be quite dry [9] and all thoroughly mixed by stirring with a warmed glass rod. Partial mixing means partial decomposition. The rod is brushed clean. The crucible is placed in a dish of cold water, taking care to keep the inside of the

[1] Cassiterite may take 45 to 60 minutes—E. S. Simpson, *Chem. News*, **99**, 243, 1909; W. B. Giles, *ib.*, **99**, 1, 25, 1909; J. Gray, *Journ. Chem. Met. Soc. S. Africa*, **10**, 312, 1910; H. Milou and R. Fouret, *Int. Cong. App. Chem.*, **8**, i, 373, 1912; J. M. Henderson, *Eng. Min. Journ.*, **103**, 267, 1917. For sintering with lime, H. W. Hutchin, *Inst. Min. Met.*, **23**, 268, 1914; S. Tamaru and N. Andô, *Zeit. anal. Chem.*, **84**, 89, 1931.

[2] Nickel crucibles are recommended for the determination of metals precipitated by hydrogen sulphide in acid solutions—tantalum, columbium, tin, etc.; silver crucibles for the determination of silica, alumina, iron, manganese, cerium, etc. According to G. Scarpa (*Atti Accad. Lincei*, (5), **24**, i, 738, 955, 1915), silver crucibles are attacked more rapidly by potassium hydroxide than by sodium hydroxide; at moderate temperatures the attack is less if oxidising agents are absent. For iron crucibles, see Noaillon, *Bull. Soc. chim. Belg.*, **28**, 212, 1914. *Cf.* Note 2, page 528.

[3] J. Darroch and C. A. Meiklejohn, *Eng. Min. Journ.*, **82**, 818, 1906; H. Angenot, *Zeit. angew. Chem.*, **17**, 1274, 1904. For opening copper pyrites by fusion with six times its weight of potassium persulphate, see L. Majewski, *Kosmos*, **35**, 597, 1910.

[4] S. W. Parr, *Journ. Amer. Chem. Soc.*, **22**, 646, 1900; **30**, 764, 1908 (coal in a steel bomb); H. H. Pringsheim, *Amer. Chem. Journ.*, **31**, 386, 1904; *Ber.*, **36**, 4244, 1903; **37**, 2155, 1904; **38**, 2436, 1905 (halogens, arsenic and phosphorus in organic compounds with a steel bomb).

[5] F. von Konek, *Zeit. angew. Chem.*, **17**, 771, 1904; F. von Konek and A. Zöhls, *ib.*, **17**, 1093, 1904; H. H. Pringsheim, *ib.*, **17**, 1454, 1904.

[6] J. H. Walton and H. A. Scholz (*Amer. Chem. Journ.*, **39**, 771, 1908; *Chem. News*, **98**, 61, 76, 1908) used zinc sulphide either alone or mixed with iron pyrites—W. B. Pollard, *ib.*, **98**, 211, 1908. There are many cases where the presence of zinc and sulphur is not particularly objectionable; in other cases such additions would present insuperable objections.

[7] S. W. Parr, *Journ. Amer. Chem. Soc.*, **24**, 167, 1902.

[8] If lead be present it will be found associated with the silica as lead sulphate.

[9] The mixture is so easily "ignited" that if any moisture be present, the heat evolved by the reaction with sodium peroxide suffices for the decomposition of the silicate.

crucible dry. The cover is placed on the crucible a little to one side, so that a piece of lighted magnesium ribbon,[1] just over 1 cm. long, may be dropped into the crucible, and the cover placed in position immediately the mixture ignites. When the mass has cooled a little, about a minute after ignition, place the crucible in a clean evaporating basin, cover with a clock-glass and add about 100 c.c. of cold water. When the violence of the reaction is over, the solution can be acidified with hydrochloric acid and the silica determined by two evaporations in the usual manner.

For comparison purposes, two samples of a frit treated by the standard process gave 30·06 and 30·04 per cent. of silica and two samples of the same frit, treated by the process just described, gave 29·98 and 30·06 per cent. of silica. The principal advantages of the method now under discussion are: (1) the vessel in which the decomposition occurs is much less attacked than usual—thus, an 18-gram crucible lost nearly 0·34 grm. in 16 fusions; [2] and (2) the whole process occupies but a few minutes. The mixing, ignition, cooling and dissolution of the melted mass can be done in about 5 minutes.

The method can be advantageously used for clays, galena,[3] lead glazes, lead slag, monazite sand, etc. If much titanium be present, a preliminary fusion with potassium bisulphate and leaching with water is recommended before the sodium peroxide fusion for tin.[4] The decomposition with basic substances like chromite, franklinite and bauxite is not satisfactory. If the presence of iron be not objectionable, chromite and franklinite can be completely decomposed by substituting 2·0 grms. of iron pyrites and 0·3 grm. of magnesium powder in place of the 1·2 grms. of powdered zinc sulphide. If the iron be objectionable, some other method of decomposition must be used. A similar remark applies to the addition of zinc sulphide.[5]

Reduction Process.—In the case of glazes containing tin oxide, it is sometimes advisable to subject the finely divided and dried material to a preliminary heating in a reducing atmosphere, as recommended by Wells,[6] in order to convert the oxide to metallic tin soluble in hydrochloric acid. The powdered material may or may not be first digested in hydrochloric acid and dried. A thin layer of the dried material is spread on the bottom of a porcelain boat— about 7 cm. long and 1 cm. broad. The boat is weighed, as usual, before and after the addition of the powder.[7] The boat is placed in a hard glass tube— about 30 cm. long and 2 cm. wide—the tube being drawn out at the end *A*,

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[1] A piece of twine about 2 cm. long, soaked in alcohol, may be used when the introduction of magnesia is not desired.

[2] For the losses with direct fusions, see page 144.

[3] The galena is itself oxidisable (combustible) and the proportion of zinc sulphide may be accordingly reduced. Thus the charge for galena may be: 0·5 grm. powdered (200's lawn) ore; 8·0 grms. of sodium peroxide; 0·8 grm. zinc sulphide; 0·3 grm. potassium persulphate. Sulphuric acid is used for neutralising the alkaline solution and sufficient acid to make about 2 per cent. excess H_2SO_4 is added. Sodium bisulphite is added to reduce the lead peroxide and the solution boiled 5 minutes to get rid of the sulphur dioxide. The lead sulphate can then be determined gravimetrically or volumetrically (molybdate process). The trial experiments were quite satisfactory.

[4] E. A. Wraight and P. L. Teed, *Inst. Min. Met.*, **23**, 280, 1914.

[5] Unless some other sulphide be available.

[6] J. S. Wells, *School Mines Quart.*, **12**, 295, 1891; *Journ. Amer. Chem. Soc.*, **20**, 687, 1898; *Chem. News*, **64**, 294, 1891; M. W. Iles, *ib.*, **50**, 194, 1884; **85**, 179, 1902; A. Hilger and H. Haas, *ib.*, **63**, 195, 1891; *Ber.*, **23**, 458, 1890; J. A. Müller, *Bull. Soc. chim.*, (3), **25**, 1004, 1901; *Chem. News*, **85**, 147, 1902; W. Hampe, *Chem. Ztg.*, **11**, 19, 1887; H. W. Rennie and W. H. Derrick, *Journ. Soc. Chem. Ind.*, **11**, 662, 1892; G. L. Mackenzie, *Trans. Inst. Min. Met.*, **13**, 87, 1903; H. Rose, *Pogg. Ann.*, **112**, 163, 1861; C. Pirlot, *Bull. fed. ind. Chim. Belg.*, **5**, 281, 1926; N. I. Matveev, *Zavodskaza Lab.*, **5**, 736, 1936.

[7] The boat funnel of Stoltzenberg is convenient for filling boats with powder.

fig. 84. The wide end of the tube is connected by means of a perforated stopper with a wash-bottle and a Kipp's hydrogen apparatus; the opposite end of the tube is allowed to dip in a beaker containing dilute hydrochloric acid (1:10). The hydrogen is passed through the wash-bottle[1]—about two bubbles per second. When the air has been expelled from the tube, the gas jet [2] is lighted, and arranged so that about 15 cm. of the tube, in the neighbourhood of the boat,
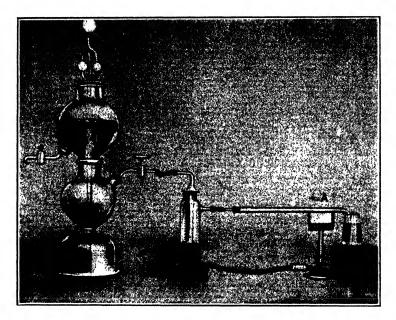
FIG. 84.—Opening Lead and Tin Silicates by a Preliminary Reduction.

is heated to a dull redness [3] for three or four hours. The boat is allowed to cool while the current of gas is still passing.[4] When cold, transfer the contents of the boat [5] to a 400 c.c. beaker and treat the mass with 100 c.c. of hydrochloric acid with a few drops of nitric acid in order to convert the stannous into stannic chloride. Let the vessel stand in a warm place until the action has subsided. Boil 3 minutes. Dilute with an equal volume of hot water and filter through a hot-water funnel (page 333). Ignite the filter-paper and contents and fuse [6] the residue with four or five times its weight of sodium carbonate and

[1] That shown in the diagram is J. Habermann's (*Zeit. anal. Chem.*, **24**, 79, 1883).

[2] A Weston's cap on an ordinary Bunsen burner is very convenient for this purpose, as shown in the diagram.

[3] The reduction of the tin oxide begins about 170°; lead oxide about 310°—W. Müller, *Pogg. Ann.*, **107**, 136, 1869. H. Haas (*Ueber die quantitative Trennung des Zinns und Titans*, Erlangen, 1890) separates tin from titanium by calcination of the mixture in a current of hydrogen, whereby tin alone is reduced to the metal and is subsequently dissolved by treatment with hydrochloric acid.

[4] Coal-gas may be used, but the sulphur compounds, present in coal-gas, may form volatile sulphides with some of the constituents of the powder.

[5] The boat should not be heated high enough to vitrify the powder.

[6] It is not safe to assume that all the reducible oxides have been reduced to the metal and dissolved in the acids. A second treatment with the gas or fusion of the residue, as described in the text, is sometimes advisable.

a gram of sodium nitrite in a platinum crucible. Take up the cold mass with hydrochloric acid and a drop of nitric acid. Mix the solution with that derived from the digestion of the "reduced" glaze with hydrochloric acid. Evaporate the solution to dryness for the separation of the silica (page 147). Nitric acid is sometimes preferred to hydrochloric acid to avoid dealing with the sparingly soluble lead chloride. If nitric acid be used with tin and antimony glazes, metastannic and antimonic acids will contaminate the silica.[1] If tin and lead be associated with the silica, alumina, magnesia, etc., precipitate the tin and lead as sulphides, as described below.

Fusion with Potassium Cyanide.—If tin and phosphorus be present, the silica may be contaminated with a metastannic phosphate (possibly $2SnO_2 . P_2O_5$).[2] In that case, the residue left after the ignition of the silica is treated with hydrofluoric acid to drive off the silica. After weighing, the residue is fused with at least three times its weight of *pure* potassium cyanide,[3] free from sulphides, in a porcelain crucible. If the crucible be rotated and tapped while hot, the separate beads of tin will unite to form a larger bead. When cold, extract with water, filter and wash the bead of metallic tin. The bead can be weighed as metal or dissolved in hydrochloric acid and added to the main solution. The difference between the weight of the tin calculated to SnO_2 and the weight of the "silica residue" may be taken as phosphoric oxide—P_2O_5. Or the filtrate from the tin can be boiled under a good hood with hydrochloric acid until the fumes of the highly poisonous cyanogen compounds have been driven off. Evaporate the solution to a small volume, and precipitate the phosphorus as usual (page 672).[4]

The objection to this process turns on the fact that some tin may be lost owing to the formation of soluble alkali stannates. According to Bloxam,[5] if the potassium cyanide contains sulphide, an insoluble tin sulphide or a soluble thiostannate may be formed. If tungsten be present, it will be found in the solution as alkali tungstate.

Fusion with Sodium Carbonate and Sulphur.—According to Miller,[6] the hydrogen reduction for the determination of tin in, say, cassiterite, gives low results, and he prefers Rose's process by fusion with sulphur and sodium carbonate. This Hoffmann conducts in the following manner:—Intimately mix 0·5 grm. of the sample with 3 grms. of a mixture of equal parts of sodium

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[1] In that case, drive off the silica with hydrofluoric acid, and fuse the residue with sodium carbonate. Add the acid solution of the fusion to the main solution.

[2] If arsenic be present, a water-insoluble metastannic arsenate soluble in hydrochloric acid may be formed.

[3] Unless the cyanide is pure, there is apt to be a loss of tin. Apparently alkali stannite or stannate is formed by interaction between the stannic oxide and the potash resulting from the hydrolysis of the cyanide.

[4] H. Rose, *Pogg. Ann.*, 110, 425, 1860; F. Oettel, *Chem. Ztg.*, 20, 19, 1896; J. A. Müller, *Bull. Soc. chim.*, (3), 25, 1004, 1901. The potassium cyanide fusion can also be used for separating the metals reduced by this agent—H. W. Rennie and W. H. Derrick, *Journ. Soc. Chem. Ind.*, 11, 662, 1892; T. Moore, *Chem. News*, 67, 267, 1893; H. Y. Loram, *Proc. Chem. Soc.*, 27, 60, 1912.

[5] C. L. Bloxam, *Journ. Chem. Soc.*, 18, 97, 1865.

[6] E. H. Miller, *Journ. Anal. App. Chem.*, 6, 441, 1892; H. Rose, *Ausführliches Handbuch der analytischen Chemie*, Braunschweig, 2, 286, 1851; H. O. Hoffmann, *Berg. Hütt. Ztg.*, 49, 342, 350, 357, 1890; *Chem. News*, 62, 157, 1890; *Tech. Quart.*, 3, 112, 261, 1890; F. Becker, *Zeit. anal. Chem.*, 17, 185, 1878; J. Mitchell, *Manual of Assaying*, London, 481, 1881; J. F. C. Abelspies, *Trans. Inst. Min. Met.*, 13, 99, 1903; H. W. Rennie and W. H. Derrick, *Journ. Soc. Chem. Ind.*, 11, 662, 1892; E. D. Campbell and E. C. Champion, *Ind. and Iron*, 267, 1898; O. Beck and H. Fischer, *School Mines Quart.*, 20, 372, 1899; *Chem. News*, 80, 259, 1899 (comparison of methods); L. Medri and C. Gastaldi, *Boll. chim. farm.*, 48, 893, 1910; A. Thürmer, *Zeit. anal. Chem.*, 73, 196, 1928.

carbonate and sulphur [1] in a 30 c.c. porcelain crucible which, in turn, is placed in a larger porcelain crucible and this in a graphite crucible which has a layer of calcined fireclay spread on the bottom, so that the top of the middle crucible is nearly on a level with the top of the graphite crucible.[2] The whole is then heated in a crucible furnace for about $1-1\frac{1}{2}$ hours at a red heat. The cold mass is treated with hot water. The tin dissolves as sodium thiostannate [3] along with some copper and iron. The latter will be precipitated by the addition of sodium sulphite to the deep brown liquid.[4] Filter, wash with water containing sodium sulphite in solution, and finally with water containing hydrogen sulphide in solution. The precipitate contains iron, copper and lead. The solution contains arsenic, antimony and tin. These can be separated as described below. The objection to this process turns on the fact that it is tedious and dirty, particularly if a re-fusion be necessary. In recent years it has been displaced by the peroxide fusion.

Hydrofluoric Acid Process.—The problem with enamels and coloured glazes is often very difficult, since many metals of both the second and third groups may be present. If tin, bismuth, antimony or arsenic be present, the hydrochloric acid evaporation for silica may cause an appreciable loss by volatilisation of the chlorides.[5] It may then be advisable to make a special decomposition for metals precipitated by hydrogen sulphide in an acid solution. This is often done with hydrofluoric acid,[6] although there is still a danger of losing antimony as fluoride. Two grams of the impalpable powder are treated with about 20 c.c. of concentrated hydrofluoric acid (40 per cent.) and an equal volume of hydrochloric acid or nitric acid in a platinum dish, and the solution taken nearly to dryness.[7] If the residue [8] does not dissolve easily in hydrochloric acid, filter off the insoluble portion and reduce it in coal-gas, as indicated above; or fuse with sodium carbonate. Take up the cold cake with hydrochloric acid and add the solution to the main filtrate. Separate the metals of the hydrogen sulphide group as indicated below.

§ 123. The Behaviour of Metals of the Hydrogen Sulphide Group in the Silica Determination.

Volatilisation of the Chlorides.

Care must be taken in boiling solutions—*e.g.* in the evaporation for silica—containing chlorides of arsenic, antimony, tin, bismuth and mercury, since serious losses may occur by the volatilisation of the chlorides. Arsenious chloride, that is, arsenic trichloride, volatilises at 130°; antimony trichloride at 223°;

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[1] H. Rose's flux is a mixture of equal parts of sulphur and sodium carbonate. Chauvenet substituted potassium carbonate for the sodium carbonate. A. Froehde (*Pogg. Ann.*, 119, 317, 1875) and E. Donath (*Zeit. anal. Chem.*, 19, 23, 1880) prefer powdered sodium thiosulphate, which has previously been fused in order to remove the water. L. Bertiaux (*Ann. Chim. anal.*, 18, 217, 1913) recommends fusing with a mixture of sodium carbonate and sodium sulphide. F. F. Gorlick, *Eng. Min. Journ.*, 102, 327, 1916.

[2] The object is to cut off the supply of air, otherwise decomposition will be incomplete.

[3] Gritty particles insoluble in water show that the action was not complete. In that case, filter, wash, dry and repeat the treatment with the residue.

[4] Containing sodium polysulphide, which dissolves some iron and copper sulphides. Sodium sulphite changes sodium polysulphide to sodium monosulphide, in which iron and copper are practically insoluble.

[5] T. M. Drown and G. F. Eldridge, *Tech. Quart.*, 5, 136, 1893.

[6] H. N. Warren, *Chem. News*, 67, 16, 1893. For opening up glasses with hydrofluoric and oxalic acids, see E. C. Sullivan and W. C. Taylor, *Journ. Ind. Eng. Chem.*, 6, 897, 1914.

[7] Watch the hydrofluoric acid for "lead" impurity.

[8] A bluish residue indicates tungsten.

and stannic chloride at 114°.   But these compounds volatilise at a much lower temperature in steam.

(1) *Tin.*—Concentrated solutions of stannic chloride in the presence of hydrochloric acid (20 per cent.) lost, during 20 minutes' boiling at 107°, nearly 0·0014 grm. of $SnCl_4$.   A solution of stannous chloride—$SnCl_2$—in hydrochloric acid can be evaporated to dryness without appreciable loss.   Hence the evaporation of stanniferous glazes, without arsenic and antimony, is best made in the presence of a reducing agent.

(2) *Antimony.*—A solution of antimony trichloride—$SbCl_3$—in hydrochloric acid (20 per cent.) may be heated to 110° without serious loss, but an appreciable quantity is volatilised at higher temperatures.   Antimony trichloride is not so volatile under these conditions as stannic chloride.   Antimony pentachloride, in hydrochloric acid (20 per cent.) solution, may be evaporated to dryness with a negligibly small loss.   If, however, a mixture of stannous chloride and antimony pentachloride be heated, the latter will be reduced and the former oxidised to the more volatile chlorides.   According to Hoffmann, the addition of, say, 12 grms. of potassium chloride [1] retards the volatilisation of these chlorides and permits their solutions to be evaporated without appreciable loss.

(3) *Arsenic.*—Arsenious chloride—$AsCl_3$—and arsenious salts in solutions containing hydrochloric acid are volatilised during evaporation and boiling in comparatively large quantities, but the arsenic salts can be evaporated to dryness with no appreciable loss.   Hence the evaporation of antimonical and arsenical solutions is best made in the presence of an oxidising agent.[2]

(4) *Mercury.*—When 30 c.c. of aqueous 0·1 to 1·0 per cent. solutions of mercuric chloride were distilled, Minozzi [3] found that when half the liquid had distilled over, the distillates contained from 0·00025 to 0·0022 grm. of mercuric chloride.   The greater the concentration of the solution, the greater the loss by volatilisation.   The error introduced into an analysis, under these conditions, may amount to 0·2 per cent.   Similar results were obtained in the presence of hydrochloric and phosphoric acids, and sodium chloride.

Separation of Insoluble Constituents with the Silica.

The silica residue may be very complex.   Insoluble tin phosphates, tin arsenates, antimony and bismuth compounds [4] may separate with the silica. The determination of the silica is therefore liable to error.   In view of these difficulties, it is better to determine the members of the hydrogen sulphide group on a separate sample by, say, the hydrofluoric acid process of decomposition, page 269.   With the portion in which the members of the hydrogen sulphide group are not being determined, losses during the evaporation for silica and after the silica has separated may be neglected.   In the analysis of stanniferous slags, containing tin in addition to the usual constituents of clays, Bailey [5] evaporates the solution from the sodium carbonate fusion to dryness

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[1] M. Hoffmann, *Beiträge zur Kenntnis der analytischen Chemie des Zinns, Antimons, und Arsens*, Berlin, 10, 1911.

[2] J. I. D. Hinds, *Inter. Cong. App. Chem.*, 8, 227, 1912; *Journ. Amer. Chem. Soc.*, 34, 811, 1912; B. J. Smart and J. T. Philpot, *Journ. Soc. Chem. Ind.*, 33, 900, 1914.

[3] A. Minozzi, *Boll. chim. farm.*, 43, 745, 1904; E. Esteve, *Chem. Ztg.*, 35, 1152, 1911; P. Bohrisch and F. Kürschner, *Pharm. Centralhalle*, 52, 1367, 1911; M. Svave, *Giorn. Farm. Chim.*, 50, 433, 1900.

[4] Also tungsten, columbium and tantalum compounds, if these elements be present.

[5] H. Bailey, *Chem. News*, 73, 88, 1896.

with 20 c.c. of concentrated nitric acid and boils the residue with 20 c.c. of concentrated hydrochloric acid.[1] The insoluble residue of stannic oxide and silica is mixed with an equal volume of water; two sticks of zinc—about $2\frac{1}{2}$ cm. long—are placed in the mixture and the whole is allowed to stand in a warm place for some time. Carefully scrape off any adherent spongy tin from the sticks of zinc; filter and wash the tin and silica and transfer the insoluble mixture back from the filter-paper into the dish. Add 10 c.c. of concentrated hydrochloric acid and a few drops of nitric acid,[2] and warm the mixture until the silica appears white. Dilute the solution, filter and wash. The silica and tungsten oxide will be found on the filter-paper;[3] the tin in the filtrate.

Dott[4] separates stannic oxide from the silica by heating the mixture with three or four times its weight of hypophosphorous acid over a Bunsen flame for about 30 minutes. The tin is converted into a stannous phosphate soluble in warm hydrochloric acid. The silica is not affected by this treatment and can be filtered off.

§ 124. The Theory of Precipitation by Hydrogen Sulphide.

The terms "soluble" and "insoluble" are purely relative. With increasing refinements in the methods of measurement, the list of substances insoluble in a given solvent becomes shorter and shorter. Many substances once said to be "insoluble" in a given solvent are known to be appreciably soluble. It is all a question of delicacy of measurement. Hence some leap beyond the domain of demonstrated fact, and say, "No substance is perfectly insoluble in water."

The method of classifying certain elements into two groups—those which form soluble and those which form insoluble sulphides in hydrochloric acid—frequently conveys wrong ideas of the properties of the sulphides. The solubility of the sulphides depends upon the concentration of the acid. For instance, if hydrogen sulphide be passed into 5 c.c. of a solution of 2 grms. of tartar emetic in 15 c.c. of hydrochloric acid (sp. gr. 1·175) and 85 c.c. of water,[5] antimony sulphide will be precipitated, but not if 12 c.c. of hydrochloric acid with no further addition of water had been used. In the one case, the reaction may be represented $2SbCl_3 + 3H_2S = Sb_2S_3 + 6HCl$; and, in the second case, $Sb_2S_3 + 6HCl = 3H_2S + 2SbCl_3$. In other words, the antimony sulphide, in the second case, is decomposed as fast as it is formed. Similarly, no lead will be precipitated by hydrogen sulphide from a solution containing over 3 per cent. of hydrochloric acid (HCl), and if the solution has 2·5 per cent. of acid, the lead will be imperfectly precipitated: part will be precipitated and a certain proportion of sulphide will be decomposed as fast as it is formed and thus remain in solution. Similarly a 5 per cent. boiling solution of hydrochloric acid will prevent the precipitation of cadmium.[6]

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[1] There is no danger of losing tin, because it is here insoluble.
[2] Just sufficient to oxidise the tungsten, if any be present.
[3] Separate by the ammonia process, page 443.
[4] D. B. Dott, *Pharm. Journ.*, 81, 585, 1908.
[5] The solution of tartar emetic will keep a couple of hours.
[6] M. Martin, *Journ. prakt. Chem.*, (1), 67, 374, 1856; C. C. Hutchinson, *Phil. Mag.*, (5), 8, 433, 1879; *Chem. News*, 41, 28, 1880; W. Manchot, *Zeit. anal. Chem.*, 67, 177, 1925. In separating cadmium from zinc by hydrogen sulphide in an acid solution, some prefer to precipitate most of the zinc with the cadmium and then digest the precipitate in a solution containing about 5·5 per cent. of hydrochloric acid without heating, but with vigorous agitation. It is claimed that the zinc passes into solution and the excess of hydrogen sulphide in the solution prevents the solution of the cadmium.

If, then, a metallic sulphide be treated with hydrochloric acid, hydrogen sulphide and a metallic chloride will be formed:

$$RS + 2HCl \rightleftharpoons RCl_2 + H_2S$$

Conversely, when a metallic chloride in aqueous solution is treated with hydrogen sulphide, the metallic sulphide and hydrochloric acid are produced:

$$RCl_2 + H_2S \rightleftharpoons RS + 2HCl$$

Hydrochloric acid thus accumulates in the solution as the action goes on. After the hydrochloric acid has attained a certain concentration, any more sulphide produced will be decomposed by the acid. There are thus two simultaneous reactions going on: (1) the formation of sulphide and hydrochloric acid; and (2) the formation of chloride and hydrogen sulphide. In further illustration, if a current of hydrogen sulphide be passed through a saturated solution of zinc chloride, part of the metal is precipitated; but when the hydrochloric acid has attained a certain concentration, the action apparently ceases because the reverse change sets in. Hence the precipitation of the zinc as sulphide will be incomplete.[1] Similar remarks apply for the other metals.

We can get more precise ideas than this. Take the case of lead chloride:

$$PbCl_2 + H_2S \rightleftharpoons PbS + 2HCl$$

When equilibrium is established,[2] the solution contains lead chloride, hydrogen sulphide and hydrochloric acid. If bracketed chemical symbols be used to represent the concentration (gram-molecules per litre) of the respective compounds *in solution*, the law of mass action [3] requires that the product of the concentration of the given chloride and concentration of the hydrogen sulphide, divided by the square of the concentration of the hydrogen chloride, shall always have the same value.[4] In symbols, for equilibrium, we have

$$\frac{[PbCl_2] \times [H_2S]}{[HCl]^2} = \text{Constant} \quad . \qquad . \qquad . \qquad . \qquad (1)$$

This agrees with facts, and when the phenomenon is described in this way, it is easy to see that if the concentration of the acid be increased, and the concentration of the hydrogen sulphide be constant, the amount of lead chloride which remains in a given solution (*i.e.* escapes precipitation) must increase in order to keep the numerical value of the ratio constant. Conversely, if it be desired to keep the amount of lead chloride in the solution as low as possible, it is necessary to keep the concentration of the acid down to a minimum value.[5] The concentration of the hydrogen sulphide in solution is practically constant (about

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[1] M. Baubigny, *Compt. rend.*, **107**, 1148, 1888; G. Chesneau, *ib.*, **111**, 269, 1890; W. Wernicke, *Pogg. Ann.*, **110**, 655, 1860; A. Prim, *Chem. Ztg.*, **41**, 414, 1917. In the case of zinc, the accumulation of hydrochloric acid can be prevented by the use of certain organic salts—ammonium or sodium acetate, sodium formate. These substances react with the hydrochloric acid, producing sodium chloride and an acetate (or formate). This is a very convenient way of substituting a weak acid—say, acetic acid or formic acid—for a strong acid—hydrochloric acid. The solubility of the zinc sulphide in, say, acetic acid is so small that inappreciable amounts of zinc remain in solution, although iron, nickel, cobalt and manganese sulphides are dissolved by the acid.

[2] At an early stage in the reaction between hydrogen sulphide and lead chloride, lead thiochloride—probably $PbS.PbCl_2$—appears to be formed, since a brick-red precipitate of this compound sometimes separates when hydrogen sulphide is passed into a solution of lead chloride in hydrochloric acid—E. H. E. Reinsch, *Journ. prakt. Chem.*, (2), **13**, 130, 1876; V. Lehner, *Journ. Amer. Chem. Soc.*, **23**, 680, 1901; F. Parmentier, *Compt. rend.*, **114**, 298, 1892.

[3] See J. W. Mellor, *Chemical Statics and Dynamics*, London, 156, 1909.

[4] Neglecting disturbances due to the presence of foreign substances in the solution.

[5] This, of course, is limited by the necessity for keeping the zinc in solution, when separating lead and zinc by this method.

0·12 gram-molecule per litre at 20°) when the gas is passing through the solution. If the concentration of the hydrogen sulphide in solution were large and the concentration of the metallic chloride in solution small, a very small excess of acid would not suffice to keep the metal in solution. It will be observed, however, that the concentration of the hydrogen sulphide under ordinary conditions is small. In consequence, a comparatively small amount of acid is sufficient to prevent the separation of sulphides of zinc, iron and manganese. This may be expressed another way: if the solubility of the hydrogen sulphide had been greater than it is, some of the metals—e.g. zinc, iron, nickel—would have been included in the "hydrogen sulphide" group; and, conversely, had the solubility of the hydrogen sulphide been less than it is, some of the present members of the "hydrogen sulphide" group would not have been there—for instance, stannous tin, lead, cadmium. These deductions have been experimentally realised by Bruni and Padoa.[1] By causing the hydrogen sulphide to react under pressure the solubility of the hydrogen sulphide in the liquid was augmented and iron, nickel and cobalt were precipitated; by working under diminished pressure, the solubility of the hydrogen sulphide in the acid liquid was reduced and cadmium was not precipitated under conditions where otherwise the sulphide would have separated.

Under ordinary conditions, the solubility [2] of the precipitated sulphides in dilute hydrochloric acid, starting with the least soluble,[3] is approximately as follows--reading from the top downwards:—

Molybdenum	Bismuth	Zinc
Platinum	Stannic tin	Titanium
Gold	Mercury	Iron
Arsenic	Cadmium	Nickel
Silver	Lead	Cobalt
Copper	Stannous tin	Manganese
Antimony		

Elements wide apart in the list can be easily separated by hydrogen sulphide in acid solution, but elements close together require a very careful adjustment of the amount of acid in solution before satisfactory separations can be made. For instance, the separation of cadmium or lead from zinc by means of hydrogen sulphide is only satisfactory when the concentration of the acid is very carefully adjusted. If too much acid be present, cadmium or lead will be imperfectly precipitated; while if too little acid be present, zinc will be precipitated with the cadmium or lead.[4] Hence, no sharp line of demarcation can be drawn between metals precipitated and metals not precipitated by hydrogen sulphide in acid solution. All depends upon the concentration of the acid.[5] This is

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[1] G. Bruni and M. Padoa, *Atti Accad. Lincei*, (5), **14**, ii, 525, 1905.
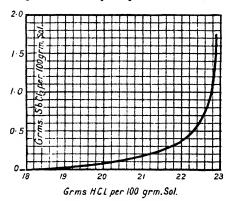
[2] The term "solubility" is here understood to refer to the amount of the element which remains in solution, or escapes precipitation, when the hydrogen sulphide is passed through an acid solution of a given concentration. The order of solubility will be the same as if the numerical values of the constants of the series indicated in equation (1), p. 272, were arranged in ascending order.

[3] The order is only approximate, and varies with the strength of the acid. For the solubility of the sulphides in water, see O. Weigel, *Zeit. phys. Chem.* **58**, 293, 1907; W. Böttger, *ib.*, **46**, 531, 1903; M. Hoffmann, *Beiträge zur Kenntnis der analytischen Chemie des Zinns, Antimons, und Arsens*, Berlin, 49, 1911; A. V. Fuller, *Journ. Ind. Eng. Chem.*, **9**, 792, 1917.

[4] A. W. Hofmann (*Liebig's Ann.*, **115**, 286, 1860; *Journ. Chem. Soc.*, **13**, 78, 1860) separates copper and cadmium sulphides with sulphuric acid (1 : 5)—the latter alone dissolves.

[5] L. Loviton (*Journ. Pharm. Chem.*, (5), **17**, 361, 1888; *Zeit. anal. Chem.*, **29**, 345, 1890) has devised a method for separating antimony and tin based upon the solubility of the sulphides in hydrochloric acid of different concentrations; and E. Neher's process (*Zeit. anal. Chem.*,

conveniently adjusted so that the lead and stannous sulphides are precipitated, while zinc sulphide remains in solution.   A solution containing 3 c.c. of hydrochloric acid (sp. gr. 1·16) per 100 c.c. will serve this purpose.[1] If more acid be present, there will be a danger of incomplete precipitation of stannous tin and lead; if less than this amount of acid be present, some zinc, iron, nickel, cobalt or manganese may be precipitated.   The adjustment of the acid cannot be perfect, but it can generally be made so that inappreciable quantities of the sulphides to be precipitated remain in solution.   This is illustrated by fig. 85, which shows the relation between the amount of antimony chloride which remains in solution in the presence of hydrochloric acid and the concentration of this acid when the solution is saturated with hydrogen sulphide.   The curve shows that for 18 grms. and less hydrochloric acid per 100 grms. of solution, very little antimony will escape precipitation.

FIG. 85.—Effect of Hydrochloric Acid on the Solubility of Antimony Sulphide.

Filtration. — In washing sulphide precipitates, say, copper sulphide in acid solution, with hydrogen sulphide water, a colourless filtrate is usually obtained.   As the concentration of the acid in the mother liquid diminishes by washing, the filtrate sometimes becomes turbid, and, in the case of copper, may be tinted green.[2]   There are several distinct actions going on. First, the sulphide is oxidised to sulphate[3]; second, the colloidal sulphides may be deflocculated (page 85); and, third, if water alone be used in the washing the dilution of the mother liquid may lead to the precipitation of some of the elements belonging to the next group, say, zinc sulphide, and so contaminate the precipitate being washed.   Hence, the washing liquid should be kept acidified.[4]

32, 45, 1893) for the separation of arsenic, antimony and tin is based on the same property. A. A. Abel and F. Field, *Journ. Chem. Soc.*, 14, 290, 1862; F. Field, *Chem. News*, 3, 114, 1861; A. H. Low, *Journ. Amer. Chem. Soc.*, 28, 1715, 1906; O. Köhler, *Arch. Pharm.*, (3), 27, 406, 1889; *Zeit. anal. Chem.*, 29, 192, 1890; G. Panajotow, *Ber.*, 42, 1296, 1909; E. Lesser, *Ueber einige Trennungs und Bestimmungs-Methoden des Arsens, des Antimons, und des Zinns*, Berlin, 1886; W. R. Lang and C. M. Carson, *Journ. Soc. Chem. Ind.*, 21, 1018, 1902; with J. C. Mackintosh, *ib.*, 21, 748, 1902; J. and H. S. Pattinson, *ib.*, 17, 211, 1898; F. Kietreiber, *Osterr. Chem. Ztg.*, (2), 13, 146, 1910; A. W. Hofmann, *Liebig's Ann.*, 115, 286, 1860; O. Bošek, *Journ. Chem. Soc.*, 67, 515, 1895; B. Brauner, *ib.*, 67, 527, 1895; J. Clarens, *Bull. Soc. chim.*, (4), 19, 154, 1916; A. Prim, *Chem. Ztg.*, 41, 414, 1917; F. A. Gooch and B. Hodge, *Amer. Journ. Sci.*, (3), 47, 382, 1894; H. Rose, *Ann. Phys. Chem.*, 107, 186, 1859; H. A. Fales, *Inorganic Quantitative Analysis*, 248, 1928; L. Lehrmann, *Journ. Chem. Educn.*, 10, 50, 1933; L. Lehrmann and H. Weissberg, *ib.*, 10, 54, 1933.

[1] A. A. Noyes and W. C. Bray, *Journ. Amer. Chem. Soc.*, 29, 137, 1907; *Tech. Quart.*, 19, 191, 1906.

[2] The filtrate becomes darker in colour, and finally flakes of copper sulphide separate from it.

[3] Hence the filtration should be conducted as rapidly as possible, and the filter-paper with the precipitate should be kept filled with the hydrogen sulphide wash-water.

[4] G. Larsen, *Zeit. anal. Chem.*, 17, 312, 1878; E. Berglund, *ib.*, 22, 184, 1883; W. Dederichs, *Pharm. Ztg.*, 44, 178, 1899.   Mineral acids are objectionable if the filter-paper is to be dried afterwards, because the acid is concentrated on the paper during the drying and the paper is attacked.   The paper then readily disintegrates.   A dilute solution of acetic acid, saturated with hydrogen sulphide, gives good results.

§ 125. The Separation of the Metals Precipitated by Hydrogen Sulphide in Acid Solutions.

In the extreme case, suppose that a qualitative examination shows that the filtrate from the silica contains antimony, arsenic,[1] lead, bismuth, cadmium, tin and copper, as well as alumina, etc. The filtrate from the silica is neutralised by adding, gradually and with constant stirring, a solution of sodium carbonate until a faint permanent precipitate is obtained. The precipitate is dissolved in a minimum quantity of dilute hydrochloric acid and then 7·5 c.c. of the concentrated acid (sp. gr. 1·16) are added for every 100 c.c. of solution. Heat the solution in an Erlenmeyer's flask at 70° to 80°, and pass hydrogen sulphide, at the rate of two bubbles per second, through the hot solution[2] for about an hour while the temperature of the solution is maintained. Let the mixture cool. When cold, add one and a half times its own bulk of water (100 c.c. becomes 250 c.c.),[3] and saturate in the cold with hydrogen sulphide passing in a slow stream for about 15 minutes. Cork the flask and let the solution stand two or three hours. Filter and wash the precipitate with a dilute acid solution containing 15 c.c. hydrochloric acid (sp. gr. 1·16) per litre and saturated with hydrogen sulphide.

The precipitate may contain lead, bismuth, copper, cadmium, arsenic, antimony and tin sulphides. The precipitate will generally be almost free from

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[1] According to F. Wöhler, more or less zinc sulphide is precipitated in the presence of arsenic acid in comparatively strongly acid solutions, but not if arsenious acid be present. For this reason, and the reason stated in the next footnote, it is well to reduce any arsenic salts, if present, to the arsenious state.

[2] Elements at the upper end of the series, page 273, are precipitated more or less imperfectly in the cold. Arsenic sulphide, for instance, continues separating a long time after the solution is saturated, hence the current of gas is continued an hour longer. The sulphides which separate from a hot solution can be filtered and washed more easily than precipitates formed in cold solutions. Arsenious acid—H_3AsO_3—reacts at once with hydrogen sulphide, forming As_2S_3; with arsenic acid—H_3AsO_4—the formation of As_2S_3 is the joint effect of three consecutive reactions: (1) the formation of thioarsenic acid—H_3AsSO_3; (2) this slowly decomposes into sulphur and arsenious acid—H_3AsO_3; (3) this latter reacts with the hydrogen sulphide, as indicated above. Hence, the initial and end products are represented by the equation: $2H_3AsO_4 + 5H_2S = As_2S_3 + 2S + 8H_2O$. One object of heating is to accelerate the very slow decomposition of the thioarsenic acid. Hence, before passing the hydrogen sulphide, some prefer to reduce the arsenic acid to arsenious acid with sulphur dioxide, or by warming the solution with a mixture of hydrochloric acid and hydriodic acid (or potassium or ammonium iodide)—sulphur dioxide is not recommended as a reducing agent—L. L. de Koninck, *Bull. Soc. chim. Belg.*, **23**, 88, 1909. There is also a very slow side reaction— $2H_3AsO_4 + 5H_2S = As_2S_5 + 8H_2O$—particularly in cold, feebly acid solutions (J. P. Bouquet and S. Cloiz, *Ann. Chim. Phys.*, (3), **13**, 44, 1845; B. Brauner and F. Tomiczek, *Journ. Chem. Soc.*, **53**, 145, 1888; *Monats.*, **8**, 607, 1887; L. R. W. McCay, *Chem. News*, **54**, 287, 1886; *Amer. Chem. Journ.*, **9**, 174, 1887; **10**, 6, 1888; *Zeit. anorg. Chem.*, **29**, 36, 1901; *Journ. Amer. Chem. Soc.*, **24**, 661, 1902; *Zeit. anal. Chem.*, **27**, 632, 1888; F. Neher, *ib.*, **32**, 45, 1893; R. Bunsen, *Liebig's Ann.*, **192**, 305, 1878; H. Rose, *Pogg. Ann.*, **107**, 186, 1859; J. J. Berzelius, *Pogg. Ann.*, **7**, 2, 1826; H. Ludwig, *Arch. Pharm.*, **147**, 32, 1859; A. Fuchs, *Zeit. anal. Chem.*, **1**, 189, 1862; B. Brauner, *Journ. Chem. Soc.*, **67**, 527, 1895; F. L. Usher and M. W. Travers, *ib.*, **87**, 1370, 1905; F. W. Küster and G. Dahmer, *Zeit. anorg. Chem.*, **33**, 105, 1902; W. Foster, *Journ. Amer. Chem. Soc.*, **38**, 52, 1916).

[3] If sulphuric acid be used in place of hydrochloric acid, use 3·75 c.c. of sulphuric acid (sp. gr. 1·84) with the same dilutions. The greater acidity of the hot solution prevents the separation of titanium hydroxide during the heating. The acid is also useful in preventing the separation of bismuth and antimony oxychlorides. The great dilution required for the separation of lead and stannous tin would lead to the precipitation of the oxychlorides in question.

aluminium, iron, zinc, nickel, cobalt and manganese.[1]   The filtrate is used for the determination of the alumina, etc. (page 157).[2]

Precipitation in Pressure Flasks.—When molybdenum, platinum, gold or selenium is present, the solution is placed in a thick-walled mineral water bottle or "pressure flask"[3] and saturated with hydrogen sulphide in the cold. A cork is then wired into the neck of the bottle, or the stopper screwed down. The pressure bottle is now suspended by a wire in a water bath so that it is clear of the bottom of the bath and is immersed up to the neck in the cold water.   The water bath is gradually heated until the water boils.   Boiling water is added to the bath, if necessary, as the water evaporates, but the fresh water should not be poured directly on the pressure bottle.   After about an hour's boiling the water bath is allowed to cool; the bottle is then removed from the bath, opened and the cold solution saturated with hydrogen sulphide. It is advisable to wrap a stout wire gauze round the bottle so that no damage may be done if it bursts during the heating.   Molybdenum, platinum, gold, selenium (also tellurium), if present, will be found with the precipitated sulphides of tin, arsenic, antimony, lead, cadmium, etc.

§ 126. The Separation of Tin, Arsenic and Antimony from the Remaining Metals.

The precipitate is now treated with a 12·5 per cent. solution (sp. gr. 1·14) of sodium monosulphide[4] in a covered beaker and heated to about 70°.   The lead, copper,[5] cadmium[6] and bismuth[7] present remain undissolved, while the arsenic, antimony and tin pass into solution.[8]   The precipitate is washed with the sodium sulphide solution.   The arsenic, antimony and tin in the solution

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[1] If the solution contains both nitric acid and barium, under certain conditions, barium sulphate may be precipitated—W. T. Hall and R. B. Woodward, *Ind. Eng. Chem. Anal. Ed.*, 6, 478, 1934.

[2] The hydrogen sulphide must be boiled off from the filtrate, and the free sulphur removed by filtration.   The iron is oxidised with a few drops of nitric acid, hydrogen peroxide or bromine water.

[3] Pressure flasks—Linter's, Salamon's—are made specially for the purpose. A. Gawalovski, *Zeit. anal. Chem.*, 22, 526, 1883; F. Allihn, *ib.*, 23, 406, 1884; R. Rempel, *Ber.*, 18, 621, 1885; A. Eiloart, *Chem. News*, 55, 148, 1887.   See also page 447.

[4] For the action of polysulphides, see H. Schiff, *Liebig's Ann.*, 115, 68, 1860.

[5] Freshly precipitated copper sulphide is appreciably soluble in colourless ammonium sulphide, and still more soluble in yellow ammonium sulphide—C. L. Bloxam, *Journ. Chem. Soc.*, 18, 94, 1865.

[6] A. Ditte (*Compt. rend.*, 85, 402, 1877; *Chem. News*, 36, 109, 1877) says that cadmium sulphide is appreciably soluble in ammonium sulphide, but E. Donath and J. Mayerhofer (*Zeit. anal. Chem.*, 20, 384, 1881) state that this is not the case.   H. Fresenius (*Zeit. anal. Chem.*, 20, 26, 1881) agrees with Ditte.   G. Vortmann, *Monats.*, 1, 952, 1880; E. Zettnow, *Pogg. Ann.*, 130, 328, 1867.

[7] T. B. Stillmann (*Journ. Amer. Chem. Soc.*, 18, 683, 1896) showed that if a solution containing bismuth be made alkaline with sodium hydroxide, and then heated with an excess of sodium sulphide, a considerable amount of bismuth remains in solution; but G. C. Stone (*ib.*, 18, 1091, 1896) pointed out that if the bismuth sulphide be first precipitated from an acid solution, it is not dissolved by subsequent treatment with an alkali sulphide.   J. Knox, *Journ. Chem. Soc.*, 95, 1760, 1909.

[8] Molybdenum, gold, platinum and selenium, if present, may be partly dissolved with the arsenic, etc., and partly retained by the insoluble sulphides.   J. J. Berzelius (*Pogg. Ann.*, 7, 4, 139, 1826) considered that arsenic pentasulphide dissolved in alkali and alkaline earth hydroxides forming arsenate and thioarsenate; rather are thioarsenate and thio-oxyarsenate formed.   L. R. W. McCay, *Chem. Ztg.*, 15, 476, 1891; *Zeit. anorg. Chem.*, 25, 459, 1900; *Ber.*, 32, 2471, 1899; R. F. Weinland and O. Rumpf, *Zeit. anorg. Chem.*, 14, 42, 1897; R. F. Weinland and P. Lehman, *ib.*, 26, 322, 1901; *Chem. Ztg.*, 23, 865, 1899; K. Preis, *Liebig's Ann.*, 257, 178, 1890; O. Klenker, *Journ. prakt. Chem.*, (2), 59, 150, 353, 1899.

are separated by the methods indicated below; the precipitate is dissolved in hydrochloric acid, and the lead, bismuth, copper and cadmium are also separated one by one, as indicated later on. If one or more of the elements in question be absent, the corresponding steps are omitted. Short cuts are also advisable in special cases.

It must also be added that, in many technical analyses, *it is not usual to work through a complex series of separations with one portion of a given sample, but several separate portions are taken and one group of constituents in each portion is determined by special methods of isolation.* For example, Lee, Trickey and Fegely [1] analyse brasses and bronzes by working on separate portions of the solution or sample as follows: (i) lead is precipitated as sulphate in the presence of tartaric acid; (ii) copper is determined volumetrically by the iodine process; (iii) tin is determined gravimetrically as stannic oxide; (iv) antimony volumetrically by permanganate in sulphuric acid solution; (v) iron gravimetrically; and (vi) zinc volumetrically with ferrocyanide in the filtrate from the iron. In a long series of separations, some of the stages may be more suited for one element than for another, and a process of analysis is selected which gives the best average for all the constituents to be determined, and not the one most suited for any particular constituent. When, however, a separate portion of the original sample is taken for the determination of each constituent, a method of separation specially favourable for that constituent can be employed.

Theoretical.—Freshly precipitated arsenic, antimonic and stannic sulphides are quickly dissolved by sodium sulphide; [2] stannous sulphide is but slowly dissolved. [3] Soluble alkali thioarsenate—Na_3AsS_4; thioantimonate—Na_3SbS_4; and thiostannate—Na_2SnS_3—appear to be formed; while arsenious and antimonious sulphides form thioarsenite, Na_3AsS_3, and thioantimonite, Na_3SbS_3, respectively. [4]

Sodium monosulphide, in aqueous solution, is partly hydrolysed or decomposed by water, forming sodium hydroxide and hydrosulphide:

$$Na_2S + H_2O \rightleftharpoons NaOH + NaHS$$

The amount of hydrolysis depends upon the concentration of the solution. In 0·1N-solution, 86·4 per cent. of the Na_2S is hydrolysed, [5] but with increasing concentrations the amount of hydrolysis is diminished. Solutions of sulphur in the alkali sulphides are much less hydrolysed than the monosulphide.

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[1] R. E. Lee, J. P. Trickey and W. H. Fegely, *Journ. Ind. Eng. Chem.*, 6, 556, 1914.

[2] R. Bunsen, *Liebig's.Ann.*, 192, 320, 1878; H. Thiele, *ib.*, 265, 65, 1891; B. Brauner and F. Tomiczek, *Monats.*, 8, 607, 1887; F. Neher, *Zeit. anal. Chem.*, 32, 45, 1893; L. R. W. McCay, *ib.*, 27, 632, 1888; 34, 725, 1895; R. Fresenius, *ib.*, 1, 192, 1862; J. J. Berzelius, *Pogg. Ann.*, 7, 1, 1826; C. Rammelsberg, *ib.*, 52, 191, 1841; C. F. Nilson, *Journ. prakt. Chem.*, (2), 14, 149, 1877; (2), 19, 170, 1879; E. E. Brownson, *Min. Eng. World*, 39, 1155, 1913; C. von Uslar, *Zeit. anal. Chem.*, 34, 391, 1895; *Chem. News*, 73, 28, 38, 1896.

[3] Hence, some use a little nitric acid with the hydrochloric acid in order to oxidise the stannous sulphide and accelerate the rate of solution.

[4] Gold and platinum sulphides, in the same group as arsenic sulphide, dissolve with difficulty in the alkali sulphide, and thus form an intermediate link between sulphides soluble and sulphides insoluble in the alkali sulphide. According to J. Riban (*Compt. rend.*, 85, 283, 1877; *Bull. Soc. chim.*, (2), 28, 241, 1877), platinum sulphide—PtS_2—alone is practically insoluble in ammonium and sodium mono- and polysulphides. In the presence of arsenic, antimony and tin sulphides, appreciable quantities of platinum and gold sulphides pass into solution, and this the more the greater the quantity of those elements present. The separation of gold and platinum, as well as molybdenum and selenium, is not therefore satisfactory by this process, since part will be found in the solution and part with the precipitate.

[5] F. W. Küster and E. Heberlein, *Zeit. anorg. Chem.*, 43, 53, 1905; J. Walker, *Zeit. phys. Chem.*, 32, 137, 1900; H. Rose, *Pogg. Ann.*, 55, 533, 1842; C. F. Sammet, *An Investigation on the Production, Precipitation and Migration of Colloids*, Boston, Mass., 1903.

This question of hydrolysis is important, because the products of hydrolysis may attack sulphides [1] which would otherwise be insoluble.   Aqueous solutions of ammonium monosulphide are more readily hydrolysed than sodium monosulphide, consequently sodium monosulphide is preferable to the ammonium salt, particularly in the presence of copper sulphide, which is slightly soluble in ammonium monosulphide.   On the other hand, the ammonium salt is nearly always used if mercury salts be present, because mercuric sulphide is insoluble in ammonium monosulphide,[2] but readily soluble in sodium or potassium monosulphide owing to the formation of a thio-salt:

$$HgS + Na_2S = Na_2HgS_2$$

Mercuric sulphide is soluble in ammonium sulphide and also more readily soluble in potassium or sodium sulphide if a little potassium or sodium hydroxide be present.[3]   The mixed solution of potassium sulphide and hydroxide separates insoluble lead, silver, bismuth and copper very sharply from arsenic, antimony and mercury.   The mercury can be precipitated from the filtrate by the addition of ammonium chloride, the arsenic and antimony remaining in solution.   The method does not work well in the presence of tin, because some tin sulphide is precipitated with the mercury sulphide and some mercury sulphide remains in solution with the tin sulphide.   When cadmium sulphide is present, mercury sulphide is but imperfectly dissolved by the mixed hydroxide-sulphide solution.[4]

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[1] This, for instance, is the case with copper sulphide in ammonium monosulphide and particularly with ammonium polysulphide.   Copper and lead are also attacked by sodium polysulphides, apparently not altogether because of the hydrolysis.   The mode of action of the polysulphides has not yet been made quite clear.   According to V. Hassreidter (*Zeit. angew. Chem.*, 18, 292, 1905), the copper can be recovered from a solution of the sulphide in, say, sodium polysulphide by boiling the solution with the cautious addition of sodium sulphite until colourless; sodium monosulphide and thiosulphate are formed, which have no solvent action on copper sulphide.

[2] But slightly soluble in ammonium polysulphide—A. Claus, *Liebig's Ann.*, 129, 209, 1863; *Chem. News*, 9, 145, 1864; C. Barfoed, *Journ. prakt. Chem.*, (1), 93, 230, 1865; *Zeit. anal. Chem.*, 3, 139, 1864; 4, 435, 1865.

[3] J. Volhard, *Liebig's Ann.*, 255, 252, 1891; A. Claus, *Liebig's Ann.*, 129, 209, 1863; *Chem. News*, 9, 145, 1864; A. Ditte, *Compt. rend.*, 98, 1271, 1884; K. Polstorff and K. Bülow, *Arch. Pharm.*, 229, 292, 1891.

[4] C. von Uslar, *Zeit. anal. Chem.*, 34, 391, 1895; *Chem. News*, 73, 28, 38, 1896; L. J. Curtman and K. Marcus, *Journ. Amer. Chem. Soc.*, 36, 1093, 1914.

CHAPTER XXI.

THE DETERMINATION OF ARSENIC.

§ 127. The Separation of Arsenic from Antimony and Tin by Distillation.

THE distillation process, proposed by Schneider and by Fyfe, depends upon the volatility of arsenious chloride.[1] If arsenic compounds be reduced to arsenious compounds in hydrochloric acid solution by ferrous sulphate, Fischer[2] showed that the arsenic may be quantitatively separated as arsenious chloride from solutions containing antimony and tin.[3] By this means arsenic may also

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[1] See page 269.

[2] E. Fischer, *Ber.*, **13**, 1778, 1880; *Liebig's Ann.*, **208**, 182, 1881; A. Classen and R. Ludwig, *Ber.*, **18**, 110, 1885; F. Hufschmidt, *ib.*, **17**, 2245, 1884; *Chem. News*, **50**, 269, 1884; W. Odling, *ib.*, **8**, 27, 1863; T. Gibb, *ib.*, **45**, 218, 1882; F. C. Schneider, *Pogg. Ann.*, **85**, 433, 1852; A. Fyfe, *Phil. Mag.*, (4), **2**, 487, 1851; *Journ. prakt. Chem.*, (1), **55**, 103, 1852; P. Jannasch and E. Heimann, *ib.*, (2), **74**, 473, 488, 1906; O. Ducru, *Compt. rend.*, **127**, 227, 1898; *Chem. News*, **78**, 73, 1898; A. Hollard and L. Bertiaux, *ib.*, **81**, 242, 1900; *Bull. Soc. chim.*, (3), **23**, 300, 1900; A. Hollard, *ib.*, (3), **23**, 292, 1900; *Chem. News*, **81**, 258, 1900; E. Azzarello, *Gazz. Chim. Ital.*, **39**, ii, 450, 1910; J. Clark, *Journ. Soc. Chem. Ind.*, **6**, 353, 1887; A. Gibb, *ib.*, **20**, 184, 1901; J. E. Stead, *ib.*, **14**, 444, 1895; Rieckher, *Zeit. anal. Chem.*, **9**, 516, 1870; J. A. Kaiser, *ib.*, **14**, 250, 1875; H. Beckurts, *Arch. Pharm.*, **222**, 653, 1884; A. Kleine, *Stahl Eisen*, **24**, 248, 1894; J. Clark, *Journ. Anal. App. Chem.*, **6**, 277, 1892; E. Ruff and F. Lehmann, *Arch. Pharm.*, **250**, 382, 1912; W. Plato, *Zeit. anorg. Chem.*, **68**, 26, 1910; W. Hartmann, *Zeit. anal. Chem.*, **58**, 148, 1919; F. A. Stief, *Journ. Ind. Eng. Chem.*, **7**, 211, 1915; F. L. Hahn and H. Wolf, *Ber.*, **57B**, 1858, 1924; W. O. Robinson, H. C. Dudley, K. T. Williams and H. G. Byers, *Ind. Eng. Chem. Anal. Ed.*, **6**, 274, 1934; H. Hager (*Pharm. Centr.*, (3), **22**, 169, 1882) claims that the use of ferrous sulphate is due to himself and not to Fischer; Rieckher, *Le Chimiste.* **2**, 140, 1866/67.

[3] Ferrous chloride, ferrous sulphate, ferrous ammonium sulphate (Classen and Ludwig) or cuprous oxide may be used. The presence of large quantities of the ferrous salt seems to prevent the well-known volatilisation of mercuric chloride with water vapour. Oxidising agents—nitric acid—should be absent, since they will oxidise the ferrous salt and make it inert. If present, nitric acid should be removed by evaporation with sulphuric acid. A little sulphuric acid does no harm. O. Piloty and A. Stock (*Ber.*, **30**, 1649, 1897) and G. T. Morgan (*Journ. Chem. Soc.*, **85**, 1001, 1904) reduce by passing a stream of hydrogen sulphide through the boiling solution. If the arsenic be all present as arsenious salt, the ferrous salt is not needed. F. A. Gooch and E. W. Danner (*Amer. J. Science*, (3), **42**, 308, 1891), F. A. Gooch and B. Hodge (*Zeit. anorg. Chem.*, **6**, 268, 1894; *Chem. News*, **70**, 23, 1894) reduce by means of potassium iodide and hydrochloric acid; F. A. Gooch and M. A. Phelps (*Zeit. anorg. Chem.*, **7**, 123, 1894) used potassium bromide and hydrochloric acid; M. Rohmer (*Ber.*, **34**, 33, 1565, 1901) reduced with sulphur dioxide; R. C. Roark and C. C. McDonnell (*Journ. Ind. Eng. Chem.*, **8**, 327, 1916) reduce with cuprous chloride; K. K. Järvinen (*Zeit. anal. Chem.*, **62**, 184, 1923) uses a mixture of hydrobromic acid and sodium sulphite; K. Röhre (*Zeit. anal. Chem.*, **65**, 109, 1924), pyrogallol; and H. B. Bishop (*Journ. Amer. Chem. Soc.*, **28**, 178, 1906) passed sulphur dioxide through the solution during the distillation and omitted the ferrous salt. This process gives good results, and can be used when the presence of iron is objectionable. C. Friedheim and P. Michaelis (*Ber.*, **28**, 1414, 1895), H. Cantoni and J. Chautems (*Archiv Sci. Phys. Nat. Genève*, (4), **19**, 364, 1905), L. Moser and F. Perjatel (*Monats*, **33**, 779, 1912), S. W. Collins (*Analyst*, **37**, 229, 1912) reduce with methyl

be separated from the other metals of the hydrogen sulphide group.[1]   Details of the modified Fischer's process are as follows:—

Oxidation of Arsenious to Arsenic Salts.—The mixed sulphides obtained in the preceding operation are transferred to a beaker. Add, say, 2 to 3 grms. of potassium chlorate and pour in *cautiously* 40 c.c. of diluted hydrochloric acid (30 c.c. of concentrated acid, 10 c.c. water). Cover the beaker with a clock-glass and heat the mixture on a water bath until decomposition is complete and all the chlorine oxides have been expelled. The object of the oxidation is to transform the volatile arsenious salts into non-volatile arsenic salts during the solution of the mixed sulphides.

Preparation for the Distillation.—Transfer the contents of the beaker to a 400 c.c. distillation flask, the side tube of which has been bent vertically downwards. Rinse out the beaker with fuming hydrochloric acid (sp. gr. 1·19) and pour the washings into the distillation flask. Add more acid until the total volume is 100–120 c.c.,[2] add 1 grm. of potassium bromide and 3 grms. of hydrazine sulphate or chloride. The side tube of the distillation flask is connected to the head of an efficient condenser, the lower end of which passes through a rubber stopper[3] nearly to the bottom of an Erlenmeyer's flask[4] containing 300 c.c. of water. The exit tube from this flask is fitted[5] with a bulb tube to act as a water seal in case any chloride escapes condensation. If the condenser be adequately cooled, this will not be needed.

The Distillation.—The flask is heated to boiling over an asbestos pad,[6] or in an oil bath with a thermometer. The distillation is allowed to proceed until the volume of the residual liquid measures 25-30 c.c. If the amount of arsenious oxide, As_2O_3, exceeds 0·3 grm. a second distillation is necessary. A temperature of $108°$–$110°$ is best.[7] A current of cold water is passed through

alcohol; P. Jannasch and T. Seidel (*Ber.*, **43**, 1218, 1910; *Journ. prakt. Chem.*, (2), **91**, 133, 1915); P. Jannasch and E. Heimann (*ib.*, (2), **74**, 437, 1906); A. Kleine (*Chem. Ztg.*, **39**, 43, 1915); J. J. T. Graham and C. M. Smith (*Journ. Ind. Eng. Chem.*, **14**, 207, 1922); C. A. Knittel (*ib.*, **14**, 460, 1922); N. Tarugi (*Gazz. Chim. Ital.*, **52**, 11., 323, 1922); A. Schleicher and L. Toussaint (*Zeit. anorg. Chem.*, **159**, 319, 1927); H. Biltz (*Zeit. anal. Chem.*, **81**, 82, 1930); H. Biltz and K. Hoehne (*ib.*, **99**, 1, 1934) reduce with hydrazine sulphate or hydrochloride and potassium bromide with excellent results. The method possesses the advantages that (1) as but little fixed salt is introduced "bumping" is avoided in the later stages of the distillation; (2) the metals in the residue can be readily determined, the hydrazine salts being destroyed by bromine or hydrogen peroxide; (3) the method works in the presence of nitrites and nitrates, which give low results with other reducing agents. M. Hoffmann (*Beiträge zur Kenntnis der analytischen Chemie des Zinns, Antimons, und Arsens*, Berlin, 15, 1911) used potassium iodide with a current of hydrogen chloride gas.

[1] F. Wöhler, *Die Mineral-Analyse in Beispeilen*, Göttingen, 223, 1861.

[2] If antimony is to be afterwards determined by the distillation process (page 281), add 50 c.c. of a solution of zinc chloride made by saturating concentrated hydrochloric acid with metallic zinc, and evaporating till the solution boils at 108° (A. Gibb, *Journ. Soc. Chem. Ind.*, **20**, 184, 1901).

[3] J. A. Scherrer (*Bur. Stand. J. Research*, **16**, 253, 1936) distils from a one-piece glass apparatus to avoid losses due to the absorption of the volatile chlorides by the rubber stoppers.

[4] L. Brandt (*Chem. Ztg.*, **33**, 1114, 1909) condemns the use of a condensing apparatus, but advocates a delivery tube with a bulb, the tube being drawn to a narrow point and dipping into water in a beaker. The beaker is kept cool by being placed in a larger beaker containing cold water. L. Moser and J. Ehrlich (*Ber.*, **55B**, 437, 1922) adopt a similar plan.

[5] All rubber tubing and stoppers should have been previously boiled with dilute potash solution to get rid of the sulphur.

[6] F. L. Hahn and H. Wolf, *Ber.*, **57B**, 1858, 1924.

[7] If the temperature of distillation exceeds 125°, some antimony, if present, will be found in the distillate—F. Platten, *Journ. Soc. Chem. Ind.*, **13**, 324, 1894. K. Röhre (*Zeit. anal. Chem.*, **65**, 109, 1924), in the absence of antimony, distils from a solution containing calcium chloride and a large excess of hydrochloric acid at 130°, but, if antimony be present, the distillation is carried out at 100° (water bath) in a current of carbon dioxide for 2 hours. K. K.

the condenser all the time the distillation is in progress. Moser and Ehrlich [1] state that most of the arsenic trichloride distils over in the first 10 minutes, the lag being due to hydrolysis—which can be minimised by adding fresh hydrochloric acid from time to time and distilling in a current of air. The latter destroys the equilibrium and sweeps out the dissolved arsenic trichloride. The addition of a salt such as potassium bromide or barium chloride, which is much less soluble in concentrated hydrochloric acid than in water, serves to "salt out" the dissolved arsenic trichloride. Hence Moser and Ehrlich recommended the use of 1·5 grms. of potassium bromide, distilling in a rapid current of air with the flask immersed up to its neck in boiling water and adding 20 c.c. of fresh concentrated hydrochloric acid at the end of every 10 minutes. About 30-40 minutes are required to distil over 0·15 to 0·20 grm. of arsenious oxide.

Determination of Arsenic in the Distillate.—The arsenic is best determined in the distillate by the volumetric process of Mohr [2] or Pearce. The arsenic may also be precipitated as sulphide by diluting the solution with hot water and saturating the boiling solution with hydrogen sulphide,[3] and it can be weighed in the form of arsenic trisulphide, silver arsenate, or magnesium pyroarsenate. The magnesium pyroarsenate process is described in the next section. If the arsenic is weighed as trisulphide, the precipitate from the hydrogen sulphide treatment is prepared as described for antimony trisulphide on page 296. The antimony and tin may be determined in the residue in the flask by precipitating the mixed sulphides of tin and antimony with hydrogen sulphide and separating these two elements as indicated on page 310.[4]

This method gives excellent results. The main objections are: (1) the need for a special apparatus; and (2) the consumption of time, especially if large quantities of arsenic are present and a second distillation is necessary. If this process be inconvenient, the arsenic may be separated from the antimony and tin as ammonium magnesium arsenate.

Järvinen (*Zeit. anal. Chem.*, **62**, 184, 1923) uses a three-bulb still head to keep back the antimony trichloride in the later stages of the distillation. F. L. Hahn and H. Wolf (*Ber.*, **57B**, 1858, 1924) and H. Biltz (*Zeit. anal. Chem.*, **81**, 82, 1930) also recommend the use of a fractionating head.

[1] L. Moser and J. Ehrlich, *Ber.*, **55B**, 437, 1922.

[2] If the solution has to stand any length of time, and Mohr's process is intended, the solution should be nearly neutralised with sodium hydroxide and an excess of sodium bicarbonate added. This retards the rate of oxidation of the solution of arsenious chloride.

[3] H. Rose, *Handbuch der analytischen Chemie*, Berlin, 343, 1829; 390, 1871; R. E. O. Puller, *Zeit. anal. Chem.*, **10**, 45, 1871; C. Friedheim and P. Michaelis, *ib.*, **34**, 505, 1895; R. Bunsen, *Liebig's Ann.*, **192**, 305, 1878.

[4] Antimony can be separated by distillation, after the arsenic, by raising the temperature of the distillation flask to 180°. The distillation of the antimony chloride begins at about 125°. Under ordinary conditions, the contents of the distillation flask would become dry and the antimony chloride would sublime on to the neck of the flask. It is therefore necessary to use a mixture in the flask which is not liable to evaporate to dryness and which does not decompose under the conditions of the experiment—A. Gibb uses a solution of zinc chloride (page 280). After the distillation of the arsenic chloride let the flask cool, change the receiver and add 20 c.c. of concentrated hydrochloric acid. Fit up the apparatus as before, gradually raise the temperature up to 200° and pass a rapid current of hydrogen chloride through the system. The antimony chloride will collect in the receiver. The antimony may be determined volumetrically by titration exactly as described for arsenic. The solution in the flask may be dissolved in hot water and the tin determined as described below. There may be a loss of stannous chloride by this process if tin be present (L. A. Youtz, *Zeit. anorg. Chem.*, **35**, 55, 1903; W. Plato, *ib.*, **68**, 26, 1910). When arsenic, antimony and tin are all present, J. A. Scherrer (*Bur. Stand. J. Research*, **16**, 253, 1936) distils over the arsenious chloride at 110°-112° in a current of carbon dioxide. Phosphoric acid is then added to hold back stannic chloride and the antimony chloride distilled over at 155°-165°, while concentrated hydrochloric acid is run into the distillation flask at the rate of 30-40 drops per minute. The non-volatile tin-phosphoric acid complex is finally broken down by adding hydrobromic acid and the tin distilled over with a mixture of hydrobromic and hydrochloric acids at 140°.

§ 128. The Separation of Arsenic from Antimony and Tin as Magnesium Ammonium Arsenate.

Theoretical.—In 1846 Levol[1] showed that a precipitate of magnesium ammonium arsenate, resembling magnesium ammonium phosphate (page 205), is obtained when a magnesium salt is added to an ammoniacal solution of an arsenate. The precipitate so obtained is slightly soluble in water—100 grms. of water dissolve 0·021 grm. of $MgNH_4AsO_4$ at 20°. The magnesium ammonium arsenate is hydrolysed by hot water forming "free arsenic acid, ammonium arsenate and magnesia": $MgNH_4AsO_4 + 2H_2O = Mg(OH)_2 + NH_4H_2AsO_4$. If an aqueous solution be evaporated to dryness and the residue calcined, some arsenic is volatilised. "In the cold, magnesium ammonium arsenate is not hydrolysed by water."

The precipitate is much less soluble in ammoniacal solutions. A 2 per cent. solution of ammonia dissolves 0·0096 grm. of the salt per 100 grms. of the solvent at 20°. In consequence, it is usual to make the precipitation in ammoniacal solution. The presence of ammonium chloride augments the solubility of the precipitate. Thus, 100 grms. of a 1·41 per cent. solution of ammonium chloride dissolve 0·0735 grm. of the anhydrous $MgNH_4AsO_4$, while 100 grms. of a 5 per cent. solution dissolve 0·113 grm. of the salt at 20°. The presence of ammonium tartrate increases the solubility of the salt. Thus, 100 grms. of a 1·5 per cent. solution of tartaric acid, feebly ammoniacal, dissolve 0·07 grm. of $MgNH_4AsO_4$. The ammonium tartrate is needed when the precipitation is made in the presence of tin and antimony salts. The solubility of the precipitate is also much reduced in alcoholic solution and consequently many prefer to make the precipitation in a solution containing both alcohol and ammonia. The precipitate is fairly soluble in acids.

To find what amount of arsenic escaped precipitation, Hoffmann[2] determined the arsenic in the filtrate after application of the method described below. Starting with solutions containing the equivalent of 0·3 grm. of tin, 0·3 grm. of antimony and arsenic as follows, the results were

As taken	.	0·05	0·05	0·15	0·15	0·3	0·3	grm.
As in filtrate	.	0·0006	0·0005	0·0008	0·0012	0·0006	0·0008	grm.

Traces only of tin and antimony were found in the precipitated magnesium ammonium arsenate. Fresenius proposed a correction for the unprecipitated magnesium arsenate—1 mgrm. arsenic per 30 c.c. of liquid. Ducru considers Fresenius' correction too small, and Virgili considers it too high. The latter recommended an allowance of 0·0012 grm. of arsenic or 0·0016 grm. of As_2O_3 per 100 c.c. of liquid, and this agrees best with Hoffmann's work.

[1] A. Levol, *Ann. Chim. Phys.*, (3), **17**, 501, 1846; *Compt. rend.*, **23**, 57, 1846; W. Hampe, *Chem. Ztg.*, **18**, 1900, 1894; J. F. Virgili, *Zeit. anal. Chem.*, **44**, 492, 1905; R. Fresenius, *ib.*, **3**, 206, 1864; G. C. Wittstein, *ib.*, **2**, 19, 1863; R. E. O. Puller, *ib.*, **10**, 63, 1871; H. Lesser, *ib.*, **27**, 218, 1888; R. Brauner, *ib.*, **16**, 57, 1877; L. F. Wood, *ib.*, **14**, 356, 1875; *Amer. J. Science*, (3), **6**, 368, 1873; F. A. Gooch and M. A. Phelps, *ib.*, (4), **22**, 488, 1906; F. Reichel, *Zeit. anal. Chem.*, **20**, 89, 1881; C. Friedheim and P. Michaelis, *ib.*, **34**, 505, 1895; *Ber.*, **28**, 1414, 1895; R. Bunsen, *Liebig's Ann.*, **192**, 305, 1878; C. Ullgren, *ib.*, **69**, 364, 1849; M. A. von Reis, *Stahl Eisen*, **9**, 270, 1885; H. Rose, *Pogg. Ann.*, **76**, 534, 1849; E. Raffa, *Gazz. Chim. Ital.*, **39**, i, 154, 1909; J. C. Brünnich and F. Smith, *Zeit. anorg. Chem.*, **68**, 292, 1910; H. Biltz, *Zeit. anal. Chem.*, **81**, 82, 1930; J. Dick, *ib.*, **93**, 429, 1933; L. W. Winkler, *Zeit. angew. Chem.*, **32**, 122, 1919; O. Ducru, *Bull. Soc. chim.*, (3), **23**, 904, 1900.

[2] M. Hoffmann, *Beiträge zur Kenntnis der analytischen Chemie des Zinns, Antimons, und Arsens*, Berlin, 1911.

Magnesium ammonium arsenate is a white crystalline solid. Its composition corresponds with $MgNH_4AsO_4.6H_2O$ when dried over sulphuric acid in a desiccator, and $MgNH_4AsO_4.\frac{1}{2}H_2O$ when dried at 100° on a water bath. When dried at higher temperatures more water and possibly some ammonia are lost. On account of the indefinite character of the hydrated salt, it is not advisable to attempt to use this substance for the final weighing, as recommended by Koehler.[1] On ignition, the salt loses ammonia and water, forming magnesium pyroarsenate—$Mg_2As_2O_7$. If the ignition be conducted at too high a temperature, the magnesium pyroarsenate appears to decompose and some arsenic oxide is volatilised. For instance, Friedheim and Michaelis[2] found that a precipitate which theoretically should have been 0·3621 grm. $Mg_2As_2O_7$ changed in weight on ignition as indicated in the following table:—

Table XLI.—Influence of Calcination on Magnesium Pyroarsenate.

Type of burner.	Time of heating. Minutes.	Weight. Grams.
Bunsen	30	0·3612
,,	60	0·3611
Blast	30	0·3602
,,	55	0·3596
,,	85	0·3587
,,	125	0·3576
,,	155	0·3572

There is thus a loss of 4 milligrams on blasting. The numbers also show that 30 minutes' calcination on a good Bunsen burner is sufficient.

The Determination.—The solution of the freshly precipitated sulphides in sodium sulphide is evaporated nearly to dryness and the residue digested with hydrochloric acid and potassium chlorate in a flask with a reflux condenser (page 306), in order to prevent loss by the volatilisation of arsenic chloride.[3] The solution should occupy about 100 c.c. Add (say, 12 grms.) tartaric acid,[4] ammonium chloride (about 2 grms. per 50 c.c.) and an excess of concentrated ammonia (one-third the total volume of the solution).[5] The arsenic is then

[1] O. Koehler, *Archiv Pharm.*, (3), **27**, 406, 1889; R. Fridli, *Pharm. Zentr.*, **67**, 241, 1926.

[2] E. W. Parnel, *Chem. News*, **21**, 133, 213, 1870; R. W. E. Maclvor, *ib.*, **32**, 283, 1875; F. Field, *ib.*, **21**, 193, 1870; *Journ. Chem. Soc.*, **26**, 6, 1873; C. Rammelsberg, *Ber.*, **7**, 544, 1874; L. Chevron and A. Droixhe, *Bull. Acad. Belg.*, (3), **16**, 475, 1888; F. Reichel, *Zeit. anal. Chem.*, **20**, 89, 1881; R. Brauner, *ib.*, **16**, 57, 1877; C. Friedheim and P. Michaelis, *ib.*, **34**, 505, 1895; M. Austin, *Zeit. anorg. Chem.*, **23**, 146, 1900; C. Lefèvre, *Ann. Chim. Phys.*, (6), **27**, 55, 1892; M. Wunder and C. Schuller, *Ann. Chim. anal.*, **18**, 221, 1913.

[3] O. Piloty and A. Stock, *Ber.*, **30**, 1649, 1897.

[4] The object of the tartaric acid is to keep the tin and antimony in solution. If much tin be present, the addition of ammonia may produce a turbidity, showing that insufficient tartaric acid is present. In that case, decant off the clear liquid, dissolve the precipitate in tartaric acid on a water bath and then mix the solutions (page 298).

[5] Some recommend the addition of one-third the volume of 95 per cent. alcohol at this stage—F. Field, *Journ. Chem. Soc.*, **26**, 6, 1873; R. E. O. Puller, *Zeit. anal. Chem.*, **10**, 57, 1871; C. R. Fresenius, *ib.*, **3**, 206, 1864; F. Reichel, *ib.*, **20**, 89, 1881; C. Friedheim and P. Michaelis, *ib.*, **34**, 505, 1895; H. Rose, *ib.*, **1**, 417, 1862; *Pogg. Ann.*, **76**, 534, 1849; L. F. Wood, *Amer. J. Science*, (3), **6**, 368, 1873; M. Austin, *ib.*, (4), **9**, 55, 1900; O. C. Beck and H. Fisher, *Chem. News*, **80**, 259, 1899; *School Mines Quart.*, **20**, 372, 1899.

precipitated from the clear ammoniacal solution by adding magnesia mixture [1] drop by drop with constant stirring. The volume of the magnesia mixture to be added is approximately one-third the total volume of the solution.[2] Let the mixture stand in a cool place for about 12 hours. Decant the clear liquid through an ignited and weighed Gooch crucible packed with asbestos. Wash with dilute ammonia water (3·5 per cent. of ammonia), first by decantation and finally transferring the precipitate to the crucible.[3] Note the volume of filtrate and washings. Dry the precipitate at about 109°. Place a crystal of ammonium nitrate in the crucible,[4] and gradually raise the temperature until the saucer containing the Gooch crucible (page 91) is bright red, but avoid too high a temperature (page 283). Cool in a desiccator and weigh as $Mg_2As_2O_7$.[5] The weight of the magnesium pyroarsenate multiplied by 0·6372 represents the corresponding amount of As_2O_3.

Except for the time taken, especially when two precipitations are made, the method is quite satisfactory. A correction of 0·0016 grm. of As_2O_3 per 100 c.c. of filtrate and washings may be allowed.

EXAMPLE.—Suppose the precipitate has been in contact with approximately 150 c.c. of liquid, and

Crucible and precipitate	10·3143 grm.
Crucible	10·0014 grm.
$Mg_2As_2O_7$	0·3129 grm.

Hence $0·3129 \times 0·6372 = 0·1994$ grm. As_2O_3. Since 100 c.c. of filtrate involves a correction of $+0·0016$ grm., we have $0·1994 + 0·0024 = 0·2018$ grm. of As_2O_3 in the given sample, which weighed 5 grms. Hence the sample has the equivalent of 4·04 per cent. As_2O_3.

The filtrate is just acidified with hydrochloric acid and saturated with hydrogen sulphide, whereby the sulphides of tin and antimony are precipitated

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[1] MAGNESIA MIXTURE.—Dissolve 56 grms. of crystallised magnesium chloride ($MgCl_2.6H_2O$) and 70 grms. of ammonium chloride in 650 c.c. of water. When all is dissolved, make the solution up to a litre with concentrated aqueous ammonia. Filter before use. The solution is about 0·5 E strength. M. Brassier, *Ann. Chim. Phys.*, (4), 7, 355, 1866; A. L. Winton, *Journ. Amer. Chem. Soc.*, 18, 445, 1896. G. Loges (*Chem. Ztg.*, 8, 1743, 1884) uses magnesium ammonium chloride, which is not hygroscopic like magnesium chloride: 70 grms. magnesium ammonium chloride; 55 grms. ammonium chloride; make up to a litre with 2·5 per cent. ammonia. Magnesia mixture acts slowly on glass bottles—L. L. de Koninck, *Chem. Ztg.*, 19, 450, 1895. O. Kuhnt (*Chem. Ztg.*, 44, 586, 1920) says that if the solution be prepared without the addition of ammonia, it can be kept for indefinite periods without the glass being attacked. The necessary excess of ammonia is added on precipitation of the arsenic acid. Magnesia mixture containing magnesium sulphate instead of magnesium chloride is liable to give precipitates contaminated with basic magnesium sulphates. See page 208.

[2] The precipitation is facilitated by the addition of a little alcohol—E. Murmann, *Oester. Chem. Ztg.*, 13, 227, 1910.

[3] Some filter here through filter-paper and dissolve the precipitate in hydrochloric acid. The magnesium ammonium arsenate is reprecipitated in order to eliminate a possible contamination of the first precipitate with magnesia, more particularly if magnesium sulphate is one of the components of the magnesia mixture.

[4] Or ignite in a current of oxygen in a Rose's crucible.

[5] If filter-paper be used, some arsenic may be lost by volatilisation. Destruction of the filter-paper by nitric acid gives good results—L. L. de Koninck (*Zeit. anal. Chem.*, 29, 165, 1890). W. Hampe prefers to dissolve the precipitate in hydrochloric acid, remove the arsenic by passing hydrogen sulphide and determine the magnesia in the filtrate by precipitating as magnesium ammonium phosphate (page 208). A better plan is to determine the arsenic volumetrically by dissolving the precipitated magnesium ammonium arsenate in acid and proceeding as indicated for Mohr's or Pearce's process. O. Bailly (*Journ. Pharm. Chim.*, (7), 20, 55, 1919), after a final washing with alcohol, titrates the magnesium ammonium arsenate directly with 0·5N-acid, using methyl orange as indicator. 1 c.c. 0·5N-acid = 0·01873 grm. As.

as indicated on page 275; or the solution may be divided into two parts and the antimony and tin determined separately, as indicated on page 301.[1]

Comparison Determinations.—In a separation of arsenic from mixed tin and antimony sulphides by this and the distillation process, the arsenic in the latter case being subsequently determined by the two processes described below, the percentage arsenic obtained was:

Levol's process.	Mohr's process.	Pearce's process.
8·25	8·25	8·15
8·30	8·29	8·19

Distillation process of separation.

§ 129. Notes on Iodine, Potassium Iodide, Starch and Sodium Thiosulphate.

In 1853, Bunsen [2] demonstrated the general applicability of reactions in which iodine was liberated from potassium iodide for volumetric analysis. Bunsen used sulphurous acid for measuring the amount of iodine set free. A. du Pasquier,[3] before Bunsen's time, brought forward the principle involved in the determination of iodine by means of sodium thiosulphate, and although the method did not give concordant results, the main difficulties were obvious after Bunsen's work. Accordingly Schwarz [4] was able to use sodium thiosulphate for titrating iodine in neutral or acid solutions, and Mohr extended the process to solutions of arsenious and antimonious salts in alkali carbonate solutions. F. Stromeyer first used starch for developing the tint of free iodine.[5] The value of the method does not rest so much on the determination of iodine in iodine compounds as on the less direct determination of those substances which liberate iodine when brought in contact with solutions of potassium iodide, *e.g.* the action of chlorine and chlorinated compounds, reductions of such substances as chromic acid, lead or manganese peroxide, ferric chloride, arsenic or antimony pentoxide, in the presence of hydrochloric acid, with or without heat. Starch, iodine, potassium iodide and sodium thiosulphate are now used so frequently in certain types of volumetric work, that some notes on the use of these substances may now be made.

Starch Solutions.

Starch is used as an indicator in titrations with iodine solutions. Free iodine colours an aqueous solution of starch blue only in the presence of a soluble iodide. The sensitiveness of the reaction is determined by the composition of the solution. The colour obtained in the presence of potassium

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[1] It will be remembered that many kinds of glass, as well as caustic alkalies, contain arsenic (page 126), but not in quantities likely to affect quantitative results by the processes here described—R. Fresenius, *Zeit. anal. Chem.*, 6, 201, 1867; W. Fresenius, *ib.*, 22, 397, 1883; J. Marshall and C. Pott, *Amer. Chem. Journ.*, 10, 425, 1888; S. R. Scholes, *Journ. Ind. Eng. Chem.*, 4, 16, 1912; A. Gautier, *Compt. rend.*, 135, 115, 1902; F. Garrigou, *ib.*, 135, 113, 1902. For the detection of arsenic and antimony in hydrochloric and sulphuric acids, see H. Koelsch, *Chem. Ztg.*, 38, 5, 1914; R. F. Tarbell, *Journ. Ind. Eng. Chem.*, 6, 400, 1914. For arsenic-free acid, see L. T. Thorne and E. H. Jeffers, *Analyst*, 31, 101, 1906; J. Habermann, *Zeit. angew. Chem.*, 10, 201, 1897; C. Busquets, *Anal. Soc. Espan. Fis. Quim.*, 34, 557, 1936.

[2] R. Bunsen, *Liebig's Ann.*, 86, 265, 1853.

[3] A. du Pasquier, *Ann. Chim. Phys.*, (2), 73, 310, 1840.

[4] C. L. H. Schwarz, *Praktische Anleitung zu Massanalysen*, Braunschweig, 1853; L. F. Kebler, *Journ. Franklin Inst.*, 153, 57, 1902.

[5] F. Stromeyer, *Schweigger's Journ.*, 12, 349, 1814.

iodide is not the same in tint as when other salts are present; also the amount of iodine needed to produce a blue colour of the same intensity is smaller with solutions of potassium iodide than with solutions of other salts of the same concentration. Sodium sulphate makes the reaction very sensitive, *e.g.* a 0·2N-solution of sodium sulphate (with starch) gives a colour with a 0·0000017N-iodine solution.[1] Some believe the blue substance is a solid solution of iodine in starch,[2] while others consider it to be an additive compound between the iodine and the starch.[3] As, however, the amount of iodine in the alleged compound is variously reported to be from 3·2 to 19·6 per cent., the formulæ representing it extend over a wide range and its existence lacks confirmation.

One gram of (preferably) potato starch is triturated with 10 c.c. of cold water until a smooth paste is obtained. Add sufficient boiling water with constant stirring to make 200 c.c. of thin translucent fluid. If the fluid be not translucent, it must be boiled one or two minutes, but prolonged boiling must be avoided, since it converts some of the starch into dextrine. Cool the solution. Let it settle overnight and decant off the clear liquid. This solution will not keep more than a couple of days. A larger quantity can be made and the clear liquid poured into small 50 c.c. phials up to the neck. The phials are placed in a water bath, heated for a couple of hours and then closed by cork stoppers. The solution so preserved will keep indefinitely. When a phial is opened, the contents deteriorate in a few days, hence the use of small bottles, which permits the solution to be used before it spoils. In order to prevent deterioration, preservatives are frequently added, *e.g.* a few drops of chloroform, oil of cassia, salicylic acid, zinc chloride, zinc iodide or mercuric chloride (2 grms. per litre of paste).[4]

Zulkowsky's[5] soluble starch is very convenient for titrations. It is sold in the form of a thick paste. A small portion is taken from the stoppered bottle on the end of a clean glass rod, and then mixed with water in a test tube for use. The so-called "soluble starch" is made by grinding, say, 100 grms. of rice starch with a 2 per cent. potash solution until a homogeneous solution is obtained. Add, with stirring, more potash solution until the volume of the mixture is from 600 to 800 c.c. Heat the mixture on a water bath until all is quite liquefied and then 30 to 40 minutes over a free flame. Filter. Add an excess of acetic acid to the filtrate. Finally precipitate the starch by adding an equal volume of 95 per cent. alcohol. Redissolve the precipitate, again precipitate the starch and dissolve the precipitate in the least possible quantity of water. Pour the solution in a thin stream into a large quantity of absolute alcohol. Filter off the precipitate and wash it with alcohol, and finally with ether. Dry *in vacuo.* The yield is about 50 or 60 per cent. "Soluble starch"

[1] J. Pinnow, *Zeit. anal. Chem.*, **41**, 485, 1902; C. Meineke, *Chem. Ztg.*, **18**, 157, 1894; A. Eckstadt, *Zeit. anorg. Chem.*, **29**, 51, 1901.

[2] F. W. Küster, *Liebig's Ann.*, **283**, 360, 1895.

[3] F. Mylius, *Ber.*, **20**, 688, 1881; C. Lonner, *Zeit. anal. Chem.*, **33**, 409, 1894; L. W. Andrews and H. M. Göttsch, *Journ. Amer. Chem. Soc.*, **24**, 865, 1902; H. B. Stocks, *Chem. News*, **56**, 212, 1887; H. Pellet, *Bull. Soc. chim.*, (2), **7**, 147, 1867; E. Baudrimont, *Répertm. Chim. Pure*, **3**, 249, 1861; R. M. Chapin, *Journ. Ind. Eng. Chem.*, **6**, 649, 1914.

[4] G. Gastine, *Bull. Soc. chim.*, (2), **50**, 172, 1888; M. Musculas, *Compt. rend.*, **78**, 1483, 1874; M. Mütnianski, *Zeit. anal. Chem.*, **36**, 220, 1897; C. Reinhardt, *ib.*, **25**, 37, 1886; F. Mohr, *ib.*, **14**, 79, 1875; A. Müller, *ib.*, **22**, 76, 1883; A. Wroblewski, *Journ. Pharm. Chim.*, (6), **8**, 314, 1907; O. Förster, *Chem. Ztg.*, **21**, 41, 1897; L. Mathieu, *Bull. Assoc. Chem. Sucr. Dist.*, **27**, 1166, 1910; A. Fernbach, *Compt. rend.*, **155**, 617, 1912; G. Rouvier, *ib.*, **114**, 749, 1892; **117**, 281, 461, 1894; C. F. Roberts, *Amer. Journ. Sci.*, (3), **47**, 422, 1894; R. M. Chapin, *Journ. Ind. Eng. Chem.*, **6**, 649, 1914; A. Ericson, *Svensk Farm. Tids.*, **20**, 499, 1916; Pollitz, *Zeit. angew. Chem.*, **30**, (1), 132, 1917.

[5] K. Zulkowsky, *Ber.*, **13**, 1395, 1874.

is a commercial article. It is sold as a white powder, which dissolves readily in boiling water, forming a clear solution. The reaction of iodine with these purified starches is sensitive and sharp.

If impure or old starch solutions be used, inaccurate results will be obtained, since such solutions contain α-amylose and hydrolytic degradation products, e.g. erythrodextrine, which give a reddish colour with iodine.[1] This colour requires an excess of thiosulphate to discharge it. If a preservative has been used with the starch, it may be necessary to be prepared for certain disturbances, e.g. the presence of zinc chloride would interfere in the titration of sulphides and carbonates. In using starch as an indicator with iodine titrations, if nitrous fumes are in the atmosphere of the laboratory, a rapid "after-blueing" of the solution may lead to high results.[2]

Potassium Iodide.

The potassium iodide used in volumetric work must be free from iodates. To test if the potassium iodide is suitable for the work, dissolve a gram of the salt in 10 c.c. of water, and add a drop of pure hydrochloric acid. If iodates be present, free iodine will be formed:

$$KIO_3 + 5KI + 6HCl = 6KCl + 3I_2 + 3H_2O$$

Shake the mixture with a little chloroform. If the chloroform shows no coloration, or, at the worst, a faint tint, the potassium iodide is suitable for the work,[3] and sufficiently free from contamination with substances which decompose potassium iodide.

Iodine.

Iodine—I. Atomic and equivalent weights: 126·92.

The most commonly used solutions are 0·1N and 0·01N, containing respectively 0·012692 and 0·001269 grm. of iodine per c.c. Since iodine is but sparingly soluble in water (about 0·03 per cent. at 18°), it is necessary to augment the solubility by using solutions of potassium iodide as a solvent for the iodine. Hence dissolve 12·692 grms. of iodine and 18 grms. of potassium iodide in about 300 c.c. of water in a litre flask, and make the

[1] F. E. Hale, Amer. J. Science, (4), 13, 379, 1902; C. Lonnes, Zeit. anal. Chem., 33, 409, 1894; C. Meineke, Chem. Ztg., 18, 157, 1894; 19, 5, 1895; G. Rivat, Chem. Ztg., 34, 1141, 1910; L. Mathieu, Ann. Chim. anal., 16, 51, 1911.

[2] F. Sinnatt (Analyst, 35, 309, 1910; 37, 252, 1912) recommends methylene blue in place of starch in titrating with standard iodine solutions. 0·05 grm. of the dye is dissolved in water, and the solution made up to 50 c.c. One c.c. of this solution per 50 c.c. of the solution to be titrated is used as indicator. The end point is indicated by a change from blue to yellowish green. It might here be added that B. Schwezoff (Zeit. anal. Chem., 44, 85, 1905) and A. Bobierre (Monit. Scient., (2), 5, 951, 1868; Chem. News, 18, 265, 1868) substitute for the starch reaction with iodine the intense red coloration furnished by the solution of iodine in pure benzene, a reaction suggested by M. Moride in 1852 (Compt. rend., 35, 789, 1852; B. M. Margosches, Zeit. anal. Chem., 44, 392, 1905). M. Bertin (Journ. de Médecine de l'Ouest, 31, 201, 1868) also used the same reaction. A. Dupré (Ann. Chim. Pharm., 94, 365, 1855) used chloroform, which is less convenient than benzene. It is claimed that the benzene reaction is 2¼ times as sensitive as starch. For the sensitiveness of iodo-starch reactions, see A. W. Lorenz, Chemist-Analyst, 19, 20, 1916.

[3] F. Pollaci, Gazz. Chim. Ital., 3, 474, 1873. This test is often prescribed for iodates, but traces of iron or cuprous oxides, in the presence of dissolved oxygen, also give the pink colour. L. W. Andrews (Journ. Amer. Chem. Soc., 31, 1035, 1909) detects iodates by using potassium hydrogen tartrate in place of hydrochloric acid; E. Deiss, Chem. Ztg., 38, 413, 1914; F. Robineau and G. Rollin, Journ. Pharm. Chim., (5), 26, 485, 1893.

solution up to a litre.[1]   The solution is standardised by decinormal sodium thiosulphate, or by means of arsenious or antimonious oxide.[2]

Commercial iodine may contain chlorine, bromine, water and cyanogen. To purify iodine [3] on a large scale, dissolve 4 kilograms of iodine in a solution containing 2 kilograms of potassium iodide, dissolved in 2 litres of water.   Pour the solution into water and let it stand until the iodine is precipitated.   The chlorine or bromine present react with the potassium iodide, liberating iodine and forming potassium chloride or bromide.   Pour off the supernatant liquid; wash the iodine with water [4] until it is free from potassium iodide; filter under suction through a layer of sand.   Transfer the iodine to a shallow dish and dry it over concentrated sulphuric acid (12 days).   Place the iodine in a combustion tube slightly inclined, with a plug of asbestos placed so as to prevent the melted iodine running down the tube.   The lower end of the combustion tube is connected with a couple of drying tubes, one containing calcium chloride and the other phosphorus pentoxide, in order to dry the air which is to pass through.   The upper end of the combustion tube passes through a rubber stopper closing a bottle, in which any iodine vapour, not previously condensed, is caught.   The stopper is fitted with a glass tube connected to an aspirator. *Slight* suction is sufficient to enable the iodine to condense far enough from the heated portion to prevent liquefaction of the sublimed crystals.   To prevent an accident from the sudden heating of the tube, place a piece of iron pipe over the part of the tube containing the asbestos and iodine, and extending about 10 cm. beyond the tube.   A layer of asbestos is placed between the glass and iron tubes.   This process is not convenient if but small quantities of iodine have to be treated.

To purify small quantities of iodine, grind, say, 6 grms. of commercial iodine with 2 grms. of potassium iodide.   Put the dry mixture in a small dry beaker (fig. 86) fitted with a Göckel's condenser.[5]   The beaker is surrounded with a cylindrical asbestos jacket (not shown in the diagram).   Place the beaker on a wire gauze or a hot plate, and heat it by means of a small flame, the condenser being full of cold water at the temperature of the room.   When violet vapours have ceased to come from the bottom of the beaker, let the apparatus cool.   A crust of iodine will be found on the condenser.   Pass a current of cold water through the condenser.   The glass contracts and the crust of iodine can be easily removed by pushing it with a glass rod into a similar beaker.   The sublimation is repeated without the potassium iodide at as low a temperature as possible.   Grind the iodine in an agate mortar, and dry in a desiccator over

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[1] A. T. Bawden and S. K. Dyche (*Ind. Eng. Chem. Anal. Ed.*, 5, 347, 1933) recommend dissolving 1 part of iodine in 2 parts of glycerol and 1 part of saturated potassium iodide solution.

[2] See next section and footnote 4, page 292.   Compare G. Vavrinecz, *Magyar Chem. Fol.*, 42, 37, 1936.

[3] L. L. de Koninck, *Bull. Assoc. Belg. chim.*, 17, 15, 1903; J. S. Stas, *Mem. Acad. Belgique*, 35, 3, 1865; *Œuvres Complètes*, Bruxelles, 1, 563, 1894; G. C. Wittstein, *Dingler's Journ.*, 200, 310, 1871; C. F. Mohr, *Lehrbuch der chemisch-analytischen Titriermethode*, Braunschweig, 269, 1874; G. P. Baxter, *Journ. Amer. Chem. Soc.*, 26, 1577, 1904; 32, 1591, 1910; A. Gross, *ib.*, 25, 987, 1903; *Chem. News*, 88, 274, 1903; L. W. Andrews, *ib.*, 90, 27, 1904; *Amer. Chem. Journ.*, 30, 428, 1903; B. Lean and W. H. Whatmough, *Proc. Chem. Soc.*, 14, 5, 1898; C. Meineke, *Chem. News*, 67, 272, 1893; *Chem. Ztg.*, 16, 1219, 1230, 1892; Z. Musset, *Zeit. anal. Chem.*, 30, 45, 1891; G. Lunge, *Zeit. angew. Chem.*, 7, 234, 1894; A. Ladenburg, *Ber.*, 35, 1256, 1902; H. Baubigny and P. Rivals, *Compt. rend.*, 137, 927, 1903; J. L. Meyer, *Amer. Journ. Pharm.*, 87, 154, 1915; G. Fouque, *Bull. Soc. chim.*, (4), 19, 270, 1916; F. C. Koehler, *Chem. Ztg.*, 39, 122, 1915; F. Lenci, *Boll. chim. farm.*, 57, 121, 1918.

[4] The washings, particularly at first, are retained and the iodide recovered.

[5] H. Göckel, *Zeit. angew. Chem.*, 12, 494, 1899.

calcium chloride—not sulphuric acid or the iodine may be contaminated.[1] If the cover of the desiccator is greased the iodine may attack the grease, forming hydriodic acid, which might contaminate the iodine.

Preservation of Iodine Solutions.—Iodine solutions should only be kept in glass-stoppered bottles—preferably made of brown glass to cut off the light. Iodine solutions diminish in strength with time, particularly if the bottle with the stock solution is frequently opened, owing to the volatilisation of the iodine. According to Schmatolla,[2] a 0·1 N-solution of iodine scarcely changes if kept for a year, particularly if the space between the stopper and the neck of the bottle be kept dry. The presence of an excess of potassium iodide lowers the vapour pressure of the iodine vapour and makes the solution keep better.[3]

FIG. 86.—Purification of Iodine.

Sodium Thiosulphate.

Anhydrous sodium thiosulphate — $Na_2S_2O_3$—molecular and equivalent weights, 158·11. Crystalline sodium thiosulphate — $Na_2S_2O_3.5H_2O$ — molecular and equivalent weights, 248·19.

The most commonly used solution is of 0·1 N-strength and contains 0·015811 grm. of the anhydrous salt or 0·024819 grm. of the hydrated salt per c.c.

This salt is much used in iodine titrations; the thiosulphate, in acid solutions,[4] is transformed by iodine into tetrathionate:

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$$

The *anhydrous* sodium thiosulphate is made by recrystallising the "pure" commercial salt from warm solutions, saturated at 30°–35°, by cooling and constant stirring. The fine-grained crystals so obtained are dried on filter-paper at the temperature of the room. The salt is then dehydrated over concentrated sulphuric acid until it has fallen to powder, and a portion heated

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[1] Iodine is not very hygroscopic, but for analytical purposes it should be protected— C. Meineke, *Chem. Ztg.*, 16, 126, 1892.

[2] O. Schmatolla, *Apoth. Ztg.*, 17, 248, 1902.

[3] WORKING UP IODINE RESIDUES.—For the recovery of iodine from laboratory residues, see H. W. Gill, *Analyst*, 38, 409, 1913; H. F. Stephenson, *ib.*, 43, 165, 1918; G. Torossian, *Journ. Ind. Eng. Chem.*, 6, 83, 1914; F. Piekenbrock, *Zeit. angew. Chem.*, 38, 331, 1925; F. Arndt, *Ber.*, 52B, 1131, 1919; I. Puig, *Quim. e Ind.*, 2, 1, 1925; F. T. van Voorst, *Chem. Weekblad*, 28, 129, 440, 1931; J. J. Hansma, *ib.*, 28, 183, 1931; W. D. Bonner and K. Masaki, *Journ. Chem. Educn.*, 7, 616, 1930; E. M. Marshall, *ib.*, 7, 1131, 1930; P. Bourcet, *Bull. Sci. pharmacol.*, 38, 365, 1931; R. F. McCleary and E. D. Degering, *Ind. Eng. Chem. Anal. Ed.*, 5, 420, 1933; M. Kleinstück and A. Koch, *Zellstoff und Papier*, 3, 361, 1923; A. Lachman, *Amer. Chem. Journ.*, 24, 31, 1900.

[4] In alkali or sodium hydrogen carbonate solutions, sodium thiosulphate and tetrathionate are partly oxidised to sulphate—G. Topf, *Zeit. anal. Chem.*, 26, 137, 277, 1887; J. P. Batey, *Analyst*, 36, 132, 1911; E. Abel, *Zeit. anorg. Chem.*, 74, 395, 1912; C. Friedheim, *Zeit. angew. Chem.*, 4, 415, 1891; I. M. Kolthoff, *Pharm. Weekblad*, 56, 572, 1919; R. M. Chapin, *Journ. Amer. Chem. Soc.*, 38, 625, 1916.

in a test tube shows no signs of fusion when heated to 50°. The dehydration is completed at 80° in an air bath with repeated stirring of the powder. For relatively small quantities, two hours will suffice. Preserve the salt in well-stoppered bottles. Young [1] finds that the salt so prepared keeps well and may be itself used for standardising iodine solutions.

A standard solution is made by weighing out the required quantity of the salt and dissolving it in the appropriate volume of water.[2] The solution should be made with water free from carbon dioxide, since the latter reacts with the thiosulphate, forming sodium sulphite and free sulphur:

$$Na_2S_2O_3 + H_2CO_3 \rightarrow Na_2SO_3 + H_2O + CO_2 + S$$

The sodium sulphite reacts with more iodine than the corresponding thiosulphate, and hence the solution appears to become more concentrated on standing. After all the carbon dioxide in the water has reacted with the thiosulphate, the solution may be kept for months without appreciable change. Treadwell found no change [3] in the titre of a solution against iodine after it had been kept for eight months. The addition of ammonium carbonate, sometimes recommended to preserve the solution, really acts in the opposite direction, and makes the solution less stable.[4]

§ 130. Mohr's Iodine Volumetric Process for Arsenic.

Theoretical.— When a solution of iodine is gradually added to a solution containing arsenious oxide, the latter is oxidised [5] to arsenic oxide, and a colourless solution of hydriodic acid is formed:

$$As_2O_3 + 2H_2O + 2I_2 = 4HI + As_2O_5$$

When all the arsenious oxide has been oxidised, any further addition of iodine

[1] S. W. Young, *Journ. Amer. Chem. Soc.*, 26, 1028, 1904; G. Topf, *Zeit. anal. Chem.*, 26, 140, 1887.

[2] For the standardisation of thiosulphate solutions, see J. L. Mayer, *Journ. Amer. Pharm. Assoc.*, 4, 690, 1915; R. M. Chapin, *Journ. Amer. Chem. Soc.*, 38, 625, 1916; W. Ponndorf, *Zeit. anal. Chem.*, 85, 1, 1931.

[3] C. Meineke, *Chem. Ztg.*, 18, 33, 1894; F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, 2, 530, 534, 1911; C. H. Hampshire and W. R. Pratt, *Pharm. Journ.*, 91, 142, 1913; A. Skrabel, *Zeit. anal. Chem.*, 64, 107, 1924; I. Yoshida, *Journ. Chem. Soc. Japan*, 48, 26, 1927; P. Bohrisch, *Pharm. Ztg.*, 59, 360, 1914.

[4] For the deterioration of sodium thiosulphate with keeping and the stabilisation of its solutions, see S. U. Pickering, *Chem. News*, 44, 277, 1881; A. H. Low, *Chemist-Analyst*, 30, 18, 1920; J. Davidsohn, *Seifensieder Ztg.*, 52, 639, 1925; F. L. Hahn and H. Windisch, *Ber.*, 55B, 3161, 1922; E. Abel, *ib.*, 56B, 1076, 1923; A. Skrabel, *Zeit. anal. Chem.*, 64, 107, 1924; C. Mayr, *ib.*, 68, 274, 1926; E. Schulek, *ib.*, 68, 387, 1926; 80, 190, 1930; F. L. Hahn and H. Clos, *ib.*, 79, 11, 1929; W. Ponndorf, *ib.*, 85, 1, 1931; R. A. Kölliker, *ib.*, 90, 272, 1932; L. B. Skinner, *Ind. Eng. Chem. Anal. Ed.*, 3, 411, 1931; E. P. Hedley, *Proc. S. Africa Sugar Tech. Assoc.*, 6th Cong., 6, 1932; F. J. Watson, *Proc. Soc. Chem. Ind. Victoria*, 32, 679, 1932; L. W. Winkler, *Pharm. Zentrh.*, 69, 24, 369, 1928; H. Rothlin, *Apoth. Ztg.*, 43, 33, 501, 1928; C. Mayr and E. Kerschbaum, *Zeit. anal. Chem.*, 73, 321, 1928. The solution should be kept in amber-coloured small glass-stoppered bottles, carefully protected from dust, air and light. It should be re-standardised frequently. For the action of acids on sodium thiosulphate, see H. von Oettingen, *Zeit. phys. Chem.*, 33, 1, 1900; A. F. Holleman, *ib.*, 33, 500, 1900.

[5] E. Waitz, *Zeit. anal. Chem.*, 10, 158, 1871; S. Avery and H. T. Beans, *Journ. Amer. Chem. Soc.*, 23, 485, 1901; J. K. Haywood, *ib.*, 25, 963, 1903; S. Avery, *ib.* 25, 1096, 1903; E. W. Washburn, *ib.*, 30, 31, 1908; F. Mohr, *Lehrbuch der chemisch-analytischen Titriermethode*, Braunschweig, 1859; J. P. Batey, *Analyst*, 36, 132, 1911; B. E. Curry and T. O. Smith, *Journ. Ind. Eng. Chem.*, 4, 198, 1912; G. S. Jamieson, *ib.*, 3, 250, 1911; L. Rosenthaler, *Zeit. anal. Chem.*, 45, 496, 1906; J. Stale, *Mitt. Lebensm. Hyg.*, 23, 72, 1932.

produces a yellow colour, or, if a solution of starch be present, blue "starch iodide" is formed. The starch solution enables one part of iodine in over three million parts of the solution to be detected. It is best to work with cold solutions, since the "starch iodide" dissociates on heating and loses its blue colour. The blue colour re-forms on cooling.

The solution should be alkaline in order to neutralise the hydriodic acid formed in the reaction. Alkali hydroxides cannot be used because they react with "starch iodide" and with free iodine ($6NaOH + 3I_2 = 5NaI + NaIO_3 + 3H_2O$); sodium carbonate is partly hydrolysed [1] in aqueous solutions ($Na_2CO_3 + H_2O = NaOH + NaHCO_3$). It therefore reacts with iodine, but to a less extent than sodium hydroxide. For example, working with a solution of iodine (1 c.c. = 0·005 grm. iodine) and a saturated solution of sodium carbonate, Waitz found:

Water	.	.	20	20	50	20	100	c.c.
Sod. carb. solution	.		5	10	10	20	20	c.c.
Iodine sol. required	.		0·25	0·3	0·35	0·8	1·1	c.c.

It is generally supposed that sodium bicarbonate does not react with iodine, and Beringer [2] quotes the following figures to show that "a large variation in the quantity of bicarbonate has no effect" on the consumption of iodine:

Sodium bicarbonate	.	.	.	1	2	5	10	grms.
Iodine solution required	.	.		20·1	20·0	20·1	20·0	c.c.

The truth is that the sodium bicarbonate is slightly decomposed in aqueous solutions, forming sodium carbonate and carbonic acid ($2NaHCO_3 = Na_2CO_3 + H_2CO_3$). The sodium carbonate is then hydrolysed, as indicated above. The amount hydrolysed is increased at elevated temperatures and in concentrated solutions.[3] Hence, in using sodium bicarbonate to neutralise the hydriodic acid, the solution should be as nearly neutral as possible at the *end* of the titration to get the best results. A deficiency of the sodium bicarbonate is very undesirable.[4] A slight excess does no serious harm, since the results will be sufficiently exact for commercial work.[5] The solution to be titrated should be dilute and cold. The titration should also be performed as quickly as possible to avoid variations in the concentration of the acid in solution by the escape of carbon dioxide.

[1] H. N. McCoy, *Amer. Chem. Journ.*, **24**, 437, 1900; A. Leclère, *Journ. Pharm. Chim.*, (7), **9**, 341, 1914.

[2] C. and J. J. Beringer, *A Textbook of Assaying*, London, 387, 1908.

[3] W. A. Puckner (*Proc. Amer. Phil. Assoc.*, **43**, 408, 1904) considers the amount of hydrolysis is also slightly greater in large flasks than in small ones owing to the escape of more carbon dioxide. The carbon dioxide is evolved during the titration by the decomposition of the carbonic acid ($H_2CO_3 = H_2O + CO_2$). Hence the titration should be made in Erlenmeyer's flasks, not in beakers.

[4] R. Kempf, *Zeit. angew. Chem.*, **30**, 71, 1917.

[5] The labour involved in the exact adjustment of the bicarbonate for "unknown" solutions might be considered "finicking" by a commercial analyst. Every 100 c.c. of 0·1N-iodine solution needs about 5 grms. of sodium bicarbonate, on the assumption that the solution is neutral before adding this amount of sodium bicarbonate. E. W. Washburn (*Journ. Amer. Chem. Soc.*, **30**, 31, 1908) avoids the disturbances with sodium bicarbonate by using 11 grms. sodium phosphate—$Na_2HPO_4.12H_2O$—for every 100 c.c. of the 0·1N-iodine solution. The sodium phosphate is supposed to be added to the neutral solution. For errors with an excess of sodium bicarbonate, see J. P. Batey, *Analyst*, **36**, 132, 1911; M. Bialobrzesky (*Zeit. anal. Chem.*, **37**, 444, 1898) recommends ammonium acetate in place of sodium bicarbonate. For the permissible limits of acidity, see I. M. Kolthoff, *Pharm. Weekblad*, **56**, 621, 1919.

The Determination.—The acid solution of the arsenious compound [1] is nearly neutralised with ammonia or sodium hydroxide.[2]   Add 20 c.c. of a saturated solution of sodium bicarbonate [3] and 2 or 3 c.c. of a solution of starch, and titrate with standard iodine solution [4] until a permanent blue tinge remains suffused through the solution.   The end-point is very sharp, and consequently the iodine must be added very gradually towards the end of the titration.[5]

EXAMPLE.—Suppose 1·5 grms. of material be under investigation and the solution requires 26·2 c.c. of iodine containing the equivalent of 0·0004092 grm. of As_2O_3 per cubic centimetre, then the material contains the equivalent of

$$0·0004092 \times 26·2 \times 100/1·5 = 0·715 \text{ per cent. of } As_2O_3$$

Correction for the Volume of the Liquid under Titration.—With the same amount of arsenic and different volumes of liquid, different volumes of the standard iodine solution may be needed to develop the starch blue.   Hence the solution to be titrated should have nearly the same concentration as the solution used for standardising the iodine.   The error is not very marked with 0·1N- and stronger iodine solutions, but with more dilute solutions, say 0·01N-, the error is quite appreciable.   *The more dilute the solution, the greater the amount of iodine needed to produce the coloration.*   Thus, Treadwell [6] found, with no potassium iodide other than that present in the standard solution:

Water	.	.	.	50	100	150	200	c.c.
0·01N-Iodine	.	.	.	0·15	0·30	0·47	0·64	c.c.

but in the presence of 1 grm. potassium iodide he found:

Water	.	.	.	50	100	150	200	500	c.c.
0·01N-Iodine	.	.	0·04	0·04	0·04	0·14	0·32	c.c.

Hence, when the volume of the solution is less than 150 c.c. and potassium iodide is present, the same amount of the iodine solution is needed to produce

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[1] If arsenic salts be present, the solution must be reduced by, say, a crystal of potassium iodide and an excess of sulphur dioxide.   The sulphur dioxide destroys the free iodine.   If all the sulphur dioxide be boiled off before the reduction is complete, the first drop of iodine from the burette in the titration will probably colour the solution yellow.   If the reduction be complete, no permanent coloration will be produced when a crystal of potassium iodide is dropped into the solution.   The solution must be boiled free from sulphur dioxide (test for sulphur dioxide as indicated page 174), but avoid prolonged boiling (page 302).

[2] The ammonia should be free from pyrrol.   This is readily obtained by tinging ammonia with potassium permanganate and afterwards decanting from any deposit formed.

[3] Free from nitrites and chlorates.

[4] STANDARD IODINE SOLUTION.—Shake, say, 1·05 grms. of resublimed iodine along with 4 grms. of potassium iodide (free from iodates) with about 20 c.c. of water in a litre flask until the iodine is dissolved.   This occupies but two or three minutes.   Make the solution up to a litre.   Standardise the solution of iodine by dissolving 0·4092 grm. of pure arsenious oxide in a hot solution containing about 20 grms. of sodium hydroxide (free from sulphur) in 100 c.c. of water (B. Penot, *Dingler's Journ.*, 127, 134, 1853; L. Müller, *ib.*, 129, 286, 1853; D. Hancock, *Journ. Amer. Chem. Soc.*, 16, 431, 1894); acidify the solution with hydrochloric acid, and then make the solution alkaline with sodium bicarbonate; cool; make the solution up to a litre.   Pipette 50 c.c. of this solution into a flask; add about 2 c.c. of starch solution and titrate with the iodine solution until the permanent blue tinge is obtained.   If 50 c.c. of the iodine solution are required, 1 c.c. of iodine solution represents 0·0004092 grm. of As_2O_3.   The solution of iodine keeps very well if stored in a cool place in the dark.

[5] Arsenites can be determined in admixture with cupric and ferric salts, since the latter do not liberate iodine from iodide in the presence of Rochelle salt and sodium bicarbonate, but under similar conditions cuprous salts are oxidised by iodine—C. D. Lander and J. J. Geake, *Analyst*, 39, 116, 1914; S. Avery and H. T. Beans, *Journ. Amer. Chem. Soc.*, 23, 485, 1901.

[6] F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, 2, 536, 1911; Eng. trans., New York, 2, 513, 1904.

the blue colour irrespective of the volume of the solution; but if the volume of the solution to be titrated be greater than 150 c.c., more iodine is necessary the greater the volume of the solution.

If the solutions to be titrated vary in volume, it is therefore necessary to apply a correction for the amount of the standard solution required to produce a coloration after the reaction between iodine and arsenious oxide is completed (compare page 181).

§ 131. Pearce's Volumetric Process for Arsenic.

In Bennett's modification of Pearce's process,[1] the compound containing the arsenic is oxidised and the arsenic oxide is precipitated as silver arsenate. The silver in the silver arsenate is determined by Volhard's volumetric process and the corresponding As_2O_3 is computed by proportion. In the older process of E. Reich (1864), the silver arsenate is determined gravimetrically, and this may be advisable when standard solutions are not available and only an occasional arsenic determination has to be made.[2]

Precipitation of Silver Arsenate.—The arsenic compound is dissolved in nitric acid—warming the solution if necessary. This oxidises the arsenious to arsenic oxide.[3] Add a few drops of phenolphthalein to the cold solution, and add sodium hydroxide until the indicator turns pink. Then add acetic acid, drop by drop, with constant stirring until the colour is discharged,[4] and add one drop of dilute acetic acid [5] in excess.[6] The solution should now occupy about 100 c.c. Add an excess, say 10 c.c., of a neutral solution of silver nitrate [7] with vigorous stirring. Let the precipitate settle a few minutes; decant the clear liquid; wash twice by decantation; and finally filter off the brick-red precipitate of silver arsenate —Ag_3AsO_4. Wash the precipitate with cold water until it is free from silver acetate and nitrate when tested with a drop of sodium chloride solution.

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[1] R. Pearce, *Proc. Colorado Scientific Soc.*, **1**, 14, 1883; *Chem. News*, **48**, 85, 1883; F. Reich and T. Richter, *Zeit. anal. Chem.*, **25**, 411, 1886; A. H. Low, *Journ. Amer. Chem. Soc.*, **28**, 1715, 1906; J. F. Bennett, *ib.*, **21**, 431, 1899; L. R. W. McCay, *Amer. Chem. Journ.*, **8**, 77, 1886; **12**, 547, 1890; *Chem. News*, **48**, 7, 168, 1883; O. J. Frost, *ib.*, **48**, 85, 1883; **53**, 221, 232, 243, 1886; T. Brown, *ib.*, **81**, 178, 184, 1900; *Journ. Amer. Chem. Soc.*, **21**, 780, 1899; R. C. Canby, *Trans. Amer. Inst. Min. Eng.*, **17**, 77, 1888/89; G. W. Lehmann and W. Mager, *Amer. Chem. Journ.*, **7**, 112, 1885; H. E. Hooper, *Eng. Min. Journ.*, **94**, 706, 1912; J. Waddell, *Journ. Ind. Eng. Chem.*, **11**, 939, 1919; W. Eschweiler and W. Röhrs, *Zeit. angew. Chem.*, **36**, 464, 1923; G. Luff, *Chem. Ztg.*, **47**, 601, 1923; L. R. W. McCay, *Journ. Amer. Chem. Soc.*, **50**, 368, 1928; B. Tougarinoff, *Bull. Soc. chim. Belg.*, **46**, 141, 1937.
[2] In that case, the silver arsenate is precipitated as described in the text, filtered and washed with a dilute solution of ammonium nitrate. The precipitate is dissolved in ammonia and the solution evaporated and dried in a weighed platinum dish. From the weight of Ag_3AsO_4 so obtained, the corresponding amount of arsenic or arsenious oxide can be readily computed.
[3] If necessary, boil to expel carbon dioxide.
[4] The precipitate formed later is soluble in nitric acid and ammonia. Nitric acid may be liberated during the separation of silver arsenate: $Na_2HAsO_4 + 3AgNO_3 = Ag_3AsO_4 + 2NaNO_3 + HNO_3$. Hence the solution must be carefully neutralised. These two reagents—nitric acid and ammonia—presented a difficulty in Pearce's original method. Canby tried to eliminate the trouble with zinc oxide. As stated in the text, Bennett used a slightly acidified solution of sodium acetate in which "silver arsenate is practically insoluble."
[5] Sodium acetate facilitates the subsequent separation of silver arsenate—C. E. Avery, *Amer. J. Science*, (2), **47**, 225, 1869.
[6] If the solution be alkaline, silver oxide may separate.
[7] SILVER NITRATE SOLUTION.—An ordinary nitric acid solution of silver nitrate will not do. Dissolve 17 grms. of silver nitrate crystals in 500 c.c. of distilled water. One c.c. will precipitate 0·005 grm. of arsenic, that is, 1 per cent. if 0·5 grm. of sample were originally taken. Hence 10 c.c. is usually an excess.

Titration for the Silver.—Dissolve the precipitate in 5–10 c.c. of dilute nitric acid (1 : 1), and collect the filtrate and washings in a beaker.[1] Dilute the solution, if necessary, to 100 c.c. with water.   Add 5 c.c. of a saturated solution of ferric ammonium alum, and titrate with a standard solution of ammonium thiocyanate[2] until a permanent red tint appears, according to Volhard's well-known process (page 65).   Shake the flask well during the titration to break up any clots of silver thiocyanate, which may enclose some of the solution to be titrated.   The process works well with small amounts of arsenic; with large quantities, the bulky precipitate is inconvenient, and silver is expensive.   Then use Mohr's process, page 290.   Phosphates and molybdates should, naturally, be absent.

§ 132. The Evaluation of Arsenious Oxide.

The amount of arsenic in commercial arsenious oxide can be determined by dissolving, say, 0·5 grm. of the sample in 20 grms. of sodium hydroxide and 100 c.c. of water.   Acidify the solution with hydrochloric acid, and add about 100 c.c. of a saturated solution of sodium bicarbonate.   Titrate with standard iodine (a more concentrated standard solution than that indicated above may be used, say that indicated on page 319).[3]

A mixture of arsenic and arsenious oxides may be treated in a similar manner.   Direct titration gives the amount of arsenious oxide.   A separate portion is similarly dissolved and the arsenic oxide (As_2O_5) is reduced[4] by boiling with an excess of hydrochloric acid and potassium iodide.   Boil the solution until all the free iodine has been driven off, and titrate the solution by Mohr's process.   This gives the total arsenious oxide.   The difference between the amount obtained in the two titrations is expressed in terms of As_2O_5 by multiplying the difference by 1·1618.

§ 133. Miscellaneous Processes.

Various methods have been proposed which are based on the direct reduction[5] of the arsenic compound to free arsenic.   The reduced arsenic is then determined volumetrically or weighed as such.

Meurice[6] adds hydrochloric acid and potassium bromide to the solution of

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[1] A white precipitate of silver chloride may remain on the filter-paper undissolved.   This can be neglected.

[2] AMMONIUM THIOCYANATE SOLUTION.—Dissolve about 8 grms. of ammonium thiocyanate in a litre of water.   Standardise the solution by titration against a 0·1N-solution of silver nitrate (acidified with nitric acid), with 5 c.c. of a saturated solution of iron alum as indicator.   The thiocyanate solution can subsequently be diluted down to 0·1N-strength; the salt is so hygroscopic that an exact quantity of it cannot accurately be weighed out.

[3] If copper is present, add 2–3 grms. sodium potassium tartrate after the sodium bicarbonate, to prevent precipitation of the copper during the titration—S. Avery and H. T. Beans, *Journ. Amer. Chem. Soc.*, 23, 485, 1901.

[4] For reduction by potassium iodide, see L. Rosenthaler, *Zeit. anal. Chem.*, 45, 596, 1906; *ib.*, 61, 222, 1922; K. and W. Böttger, *ib.*, 70, 97, 209, 1927; H. Heinrichs, *Glastech. Ber.*, 4, 130, 1926; for reduction with hydriodic acid, F. A. Gooch and P. E. Browning, *Amer. J. Science*, (3), 39, 188, 1890; (3), 40, 66, 1890; E. T. Allen and E. G. Zies, *Journ. Amer. Cer. Soc.*, 1, 739, 1918; for reduction with sulphur dioxide, L. R. W. McCay, *Amer. Chem. Journ.*, 7, 373, 1885.

[5] For reduction by hypophosphorous acid, see R. Engel and J. Bernard, *Compt. rend.*, 122, 390, 1896; by sodium hypophosphite, see L. Brandt, *Chem. Ztg.*, 37, 1445, 1471, 1496, 1913; *ib.*, 38, 984, 1914; by stannous chloride, see L. Andrews, *Chem. Ztg.*, 38, 983, 1914; R. Fridl, *Pharm. Zentrh.*, 67, 241, 1926; by titanous chloride, see A. Oliverio, *Ann. Chim. applicata*, 21, 211, 1931.

[6] R. Meurice, *Ann. Chim. anal.*, 3, 85, 1921.

arsenious arsenic and titrates with a standard solution of potassium dichromate in a current of air. The arsenic is oxidised to the pentavalent state and one drop of dichromate in excess liberates bromine, which is carried by the current of air into a test tube containing starch-potassium iodide solution.

Polyakov and Kolokolov [1] have worked out a colorimetric process, based on Feigl's test for arsenic.[2]

[1] A. Polyakov and N. Kolokolov, *Biochem. Zeit.*, **213**, 375, 1929. Compare H. J. Morris and H. O. Calvery, *Ind. Eng. Chem. Anal. Ed.*, **9**, 447, 1937.

[2] For a review of the methods for determining arsenic, see W. Dehio, *Zeit. anal. Chem.* **99**, 50, 1934; M. Horn, *Zeit. Disinfekt. Gesundh.*, **23**, 365, 1931.

CHAPTER XXII.

THE DETERMINATION OF ANTIMONY.[1]

§ 134. Antimony Sulphide.

ANTIMONY sulphide is fairly soluble in hydrochloric acid [2] containing over 20 per cent. HCl, as indicated on page 274. Hence it is necessary to work with dilute solutions if all the antimony is to be separated as sulphide. If the solution be too dilute, antimony oxychloride will separate. It is therefore best to work with a solution sufficiently acid, say 20 per cent. HCl, in order to prevent the precipitation of the oxychloride. The acid solution is saturated with hydrogen sulphide, then diluted with, say, an equal volume of water, and again saturated with the gas,[3] as indicated on page 275.

At low temperatures, and particularly with rapid streams of hydrogen sulphide, the pentasulphide, Sb_2S_5, is precipitated.[4] The higher the temperature and the slower the stream of gas, the greater the amount of trisulphide, Sb_2S_3, mixed with the pentasulphide.[5] In general work, therefore, we may assume that the precipitate will be a mixture of the two sulphides along with free sulphur. The precipitated sulphide is either red and amorphous or grey and crystalline; which it is depends on such factors as the temperature of precipitation and concentration of solution. The grey precipitate is dense and compact and it filters and washes much more rapidly than the bulkier red precipitate. It is probable that the latter has more the character of a hydro-sulphide, $Sb(HS)_3$, and the former that of the anhydrous sulphide, Sb_2S_3. When much tartaric acid is present, the precipitate is usually red.

The Influence of Chlorides.—The precipitated antimony sulphide, Sb_2S_3, almost invariably contains chlorine, which has usually been attributed to imperfect washing.[6] Part of the chlorine is evolved as hydrogen chloride when

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[1] For a bibliography of the analysis of antimony, see E. R. Darling, *Chem. Eng.*, 27, 11, 63, 1919.

[2] J. Lang, *Ber.*, 18, 2714, 1885; J. Theile, *Liebig's Ann.*, 263, 361, 1891; *Zeit. anal. Chem.*, 30, 473, 1891; T. Wilm, *ib.*, 30, 428, 1891; O. Bošek, *Chem. News*, 71, 195, 1895; B. Brauner, *ib.*, 71, 196, 1895; M. Berthelot, *Compt. rend.*, 102, 22, 84, 86, 1886; A. Ditte, *ib.*, 102, 168, 212, 1886; G. C. Wittstein, *Vierteljahr. prakt. Pharm.*, 18, 531, 1869; E. E. Brownson, *Min. Eng. World*, 39, 1155, 1913.

[3] If the solution be too acid, the clear filtrate will become turbid as soon as it comes in contact with water—say a moist beaker. In that case the solution must be diluted with water and refiltered.

[4] When the amount of hydrochloric acid in solution exceeds 10 per cent., the greater the amount of hydrochloric acid, the greater the proportion of pentasulphide precipitated.

[5] Dark brown Sb_2S_5 is precipitated from cold solutions of antimonic salts, but not from antimonious salts, by an excess of hydrogen sulphide in aqueous solution.

[6] A. Duflos, *Schweigger's Journ.*, 67, 270, 1833; H. Rose, *Pogg. Ann.*, 28, 481, 1833; 98, 455, 1856; A. Fischer, *Zeit. anorg. Chem.*, 42, 363, 1904; E. G. Beckett, *Beitrag zur Bestimmung des Antimons*, Zurich, 1909; *Chem. News*, 102, 101, 1910; O. Petricicolli and M. Reuter, *Zeit. angew. Chem.*, 14, 1179, 1901; L. A. Youtz, *Journ. Amer. Chem. Soc.*, 30, 975, 1908; J. P. Cooke, *Proc. Amer. Acad.*, 13, 27, 1877.

the sulphide is heated to 300°, and hence Beckett infers it is not all present as adsorbed hydrogen chloride; the other part of the chlorine is lost as antimony chloride when the sulphide is melted. Beckett calls the former "volatile chlorine" and the latter "fixed chlorine." In antimony sulphide, precipitated by Clarke and Henz's process, Beckett found

Volatile chlorine.	Fixed chlorine.	Ratio.
0·81 per cent.	0·30 per cent.	$2\frac{2}{3}:1$

and believes that the precipitated sulphide is a mixture of antimony hydro-sulphide, $HS - Sb\diagup^{HS}_{\diagdown HS}$, with mono- and di-chlorohydrosulphides, $HS - Sb\diagup^{Cl}_{\diagdown HS}$

and $HS - Sb\diagup^{Cl}_{\diagdown Cl}$. On heating to 300° he considers that the first decomposes into Sb_2S_3 and H_2S, while the monochlorohydrosulphide gives Sb_2S_3 and a mixture of HCl and H_2S or $SbSCl$ and H_2S

$$2HS - Sb\diagup^{Cl}_{\diagdown HS} = Sb_2S_3 + 2HCl + H_2S \quad \text{or} \quad HS - Sb\diagup^{Cl}_{\diagdown HS} = SbSCl + H_2S$$

and the dichlorohydrosulphide gives $SbSCl$ and HCl:

$$HS - Sb\diagup^{Cl}_{\diagdown Cl} = SbSCl + HCl$$

Although the red sulphide precipitate, dried at 110°, retains more "chlorine" than the grey sulphide, Beckett considers that "this is without influence," because in either case the same amount of sulphide is finally obtained. After the precipitate has been heated to 300° in a current of carbon dioxide, virtually all but 0·15 to 0·3 per cent. of the "fixed" chlorine is driven off and this amount has no appreciable influence on the result. If desired, a chlorine-free sulphide can be made by melting the sulphide in a stream of hydrogen sulphide.

The Ignition of Antimony Sulphide.—When the antimony is to be weighed as trisulphide, the excess of sulphur is removed from the precipitate by washing with, say, carbon disulphide, and the precipitate is thoroughly dried in a neutral atmosphere, say, carbon dioxide. In illustration, a precipitate of trisulphide, after drying 4 hours at 110°, weighed 0·5861 grm.; after washing with carbon disulphide and alcohol, and drying at 150° for two hours, 0·5552 grm.; again washing with carbon disulphide, and drying one hour at 180°, 0·5547 grm. Further drying for an hour at the temperatures indicated gave the following results:

Temperature	.	200°	220°	250°	280°	300°
Weight	.	.	0·5540	0·5538	0·5526	0·5523	0·5516 grm.

the weight then remaining practically constant.

Influence of Oxalic Acid.—The addition of oxalic acid to a solution of antimony or tin, feebly acid with hydrochloric acid, produces a white precipitate of antimony or tin oxalate; if the solution be alkaline, fairly soluble double oxalates are formed and the solution will remain clear, without turbidity, provided sufficient alkali be present. Hydrogen sulphide produces an orange to grey coloured precipitate of antimony trisulphide in solutions of an antimonious salt; and in solutions of a stannous salt, a black precipitate of stannous

sulphide.[1] In the presence of oxalic acid, antimonic sulphide is precipitated, while stannic salts are imperfectly precipitated, by hydrogen sulphide. If the solution be hot, and a sufficient excess of oxalic acid be present, the stannic sulphide is not precipitated at all.[2]

Influence of Tartaric Acid.—When the above reaction is used for the separation of antimony and tin, it is necessary to oxidise the stannous salts to the stannic state. This is conveniently done by means of hydrogen peroxide. Tin, however, may be carried down with the antimony sulphide. Hence the precipitate must be dissolved in sodium sulphide, more oxalic acid added and the antimony sulphide again precipitated. *The preliminary addition of an excess of tartaric acid prevents the precipitation of tin along with antimony sulphide* and renders a second precipitation unnecessary. This is the principle upon which Clarke and Henz's process [3] for the separation of tin and antimony is founded. H. Rose pointed out that the presence of tartaric acid also retards the separation of chloride—possibly SbOCl or SbSCl—with the precipitate. The chloride, if present, volatilises when the precipitate is heated to 300° in a stream of carbon dioxide and thus leads to low results [4] (see page 296). The greater the amount of tartaric acid in the solution, the less the danger of loss from this cause. Thus, with the precipitate from a gram of antimony the loss on ignition was as follows:

| Tartaric acid used | . | . | . | 0 | 2·5 | 5·5 | grms. |
| Loss on ignition | . | . | . | 0·37 | 0·18 | 0·05 | per cent. |

§ 135. The Gravimetric Separation of Antimony and Tin— Clarke and Henz's Process.

Preparation of the Solution for the Precipitation.—Dissolve, say, the mixed sulphides containing less than the equivalent of 0·3 grm. of the mixed metals in a solution of sodium or potassium sulphide (page 276) in a 500 c.c. beaker.

[1] Stannous sulphide is brown; stannic sulphide, yellow; a mixture of the two, maroon colour. C. F. Barfoed, *Zeit. anal. Chem.*, 7, 260, 1868; T. Scheerer, *Journ. prakt. Chem.*, (2), 3, 472, 1871; A. Carnot. *Compt. rend.*, 103, 258, 1886.

[2] G. Vortmann and A. Metzl (*Zeit. anal. Chem.*, 44, 525, 1905) and Mlle. Mouret and J. Barlot (*Bull. Soc. chim.*, (4), 29, 743, 1921) use phosphoric acid in place of oxalic acid to keep the tin in solution; M. Huybrechts (*Bull. Soc. chim. Belg.*, 27, 66, 1913), sodium pyrophosphate, $Na_4P_2O_7$; A. Kling and A. Lassieur (*Compt. rend.*, 170, 1112, 1920), hydrofluoric acid. According to G. Luff (*Chem. Ztg.*, 45, 229, 1921; 47, 601, 1923), A. Prim (*ib.*, 41, 414, 1917) and A. Thürmer (*Zeit. anal. Chem.*, 73, 196, 1928), antimony sulphide can be precipitated free from tin in the presence of a sufficient excess of hydrochloric acid. See also E. Winkler, *Bull. Soc. chim. Belg.*, 42, 503, 1933.

[3] F. W. Clarke, *Amer. J. Science*, (2), 49, 48, 1870; *Chem. News*, 21, 124, 1870; *Zeit. anal. Chem.*, 9, 487, 1870; 21, 114, 1882; A. Rössing, *ib.*, 41, 1, 1902; G. Vortmann and A. Metzl, *ib.*, 44, 525, 1905; E. Lesser, *ib.*, 27, 218, 1888; J. A. Müller, *ib.*, 34, 171, 1895; A. Czerwek, *ib.*, 45, 505, 1906; F. Henz, *Zeit. anorg. Chem.*, 37, 1, 1903; A. Fischer, *ib.*, 42, 372, 1904; A. Gutbier and C. Brunner, *Zeit. angew. Chem.*, 17, 1137, 1904; C. Ratner, *Chem. Ztg.*, 26, 873, 1902; J. Clark, *Journ. Soc. Chem. Ind.*, 15, 255, 1896; R. Bunsen, *Liebig's Ann.*, 192, 317, 1878; *Zeit. anal. Chem.*, 18, 264, 1879; A. Carnot, *Compt. rend.*, 103, 258, 1886; *Chem. News*, 54, 89, 1886; H. N. Warren, *ib.*, 62, 216, 1890; G. C. Wittstein and A. B. Clark, *Vierteljahr. prakt. Pharm.*, 19, 551, 1870; F. P. Dewey, *Amer. Chem. Journ.*, 1, 244, 1879; *Chem. News*, 40, 257, 1879; O. Klenker, *Journ. prakt. Chem.*, (2), 59, 353, 1899; T. Brown, *Journ. Amer. Chem. Soc.*, 21, 780, 1899; *Chem. News*, 81, 178, 184, 1900; C. Hallmann, *Vergleichende Untersuchung über Methoden der quantitativen Antimon bestimmung*, Aachen, 1911; A. Inhelder, *Beitrag zur Trennung des Antimons und Zinns und zur Analyse von Lagermetallen*, Zürich, 1911; P. Wenger and G. Paraud, *Ann. Chim. anal. Chim. appl.*, 5, 230, 1923; P. E. Winkler, *Bull. Soc. chim. Belg.*, 41, 115, 1932.

[4] H. Rose, *Pogg. Ann.*, 98, 455, 1856; O. Petriccioli and M. Reuter, *Zeit. angew. Chem.*, 14, 1179, 1901; L. A. Youtz, *Journ. Amer. Chem. Soc.*, 30, 975, 1908.

Add 6 grms. of the purest potassium hydroxide [1]; 3 grms. of tartaric acid [2]; and as much hydrogen peroxide (30 per cent.) as is necessary to decolorise the solution. Then add a volume of hydrogen peroxide equal to that already added. Boil the solution for a few minutes until the evolution of oxygen is over and the thio-salt is oxidised.[3] Cool. Cover the beaker with a clock-glass; add 15 grms. of pure oxalic acid.[4] Carbon dioxide comes off vigorously. Boil the solution briskly for 10 minutes to decompose the hydrogen peroxide completely. The solution, now occupying about 80 or 100 c.c., is allowed to cool.

Precipitation of Antimony Sulphide.—Pass a rapid current of hydrogen sulphide through the cold solution and then heat it to the boiling-point, all the time maintaining the current of hydrogen sulphide. Keep the flask or beaker in a boiling water bath.[5] After about 15 minutes dilute the solution to about 250 c.c. Continue the current of gas another 15 minutes. Remove the source of heat and continue the current of gas another 10 minutes longer. Let the precipitate settle until the solution is cold.

Washing the Precipitate.—Decant the dense precipitate of antimony sulphide through a Gooch crucible [6] which has been heated to about 300° in a stream of carbon dioxide for about an hour before cooling in the desiccator and weighing. Wash the precipitate twice by decantation with a 1 per cent. solution of oxalic acid and twice by decantation with very dilute acetic acid. Both washing liquids should be boiling and kept saturated with hydrogen sulphide.[7] The filtering and washing should be done as quickly as possible, since the antimony sulphide is liable to decompose or deflocculate and pass into solution.[8] The precipitate will be contaminated with some sulphur. It is best to remove [9] most of the sulphur by washing three times with alcohol, then with a mixture of equal parts of alcohol and carbon disulphide, again with alcohol, and finally with ether.

The Ignition of the Precipitate.—Dry the precipitate and heat it gradually to between 250° and 300° in a stream of carbon dioxide for between 30 and 60 minutes. The heating is conveniently done in Paul's drying oven,[10] fig. 87.

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[1] That is, one-third the sum of the weights of the mixed tartaric and oxalic acids. Use potassium hydroxide "pure by alcohol."

[2] That is, 10 times the maximum weight of the mixed metals—tin and antimony—in the solution.

[3] All the peroxide cannot be decomposed at this stage.

[4] That is, 50 times the weight of the mixed metals in the solution. The hot solution should be saturated with oxalic acid.

[5] If the solution be kept cold, the antimony sulphide will be difficult to filter so as to form a clear solution; if the gas be passed at once into the boiling solution, the precipitate is liable to stick tenaciously to the sides of the beaker, whereas if the gas be passed into the cold solution and the solution gradually heated to boiling during the passage of the gas, the precipitate is granular and washes easily—S. P. Sharples, *Amer. J. Science*, (2), **50**, 248, 1870; *Chem. News*, **22**, 259, 1870.

[6] If arsenic be present, it too will be precipitated as sulphide. Filter tubes, figs. 32 *B* and *C*, can be used. W. Gibbs and E. R. Taylor, *Amer. J. Science*, (2), **44**, 215, 1867; R. Fresenius, *Zeit. anal. Chem.*, **8**, 155, 1869.

[7] At this stage the antimony can usually be determined volumetrically, with a great saving in time, if a standard solution is ready.

[8] C. Friedheim and P. Michaelis, *Zeit. anal. Chem.*, **34**, 505, 1895; J. Theile, *ib.*, **30**, 479, 1891. The treatment described in the text is better than washing with carbon disulphide alone, since the latter may be entangled with the precipitate, and not pass through the filter-paper. Antimonic sulphide, Sb_2S_5, is not decomposed into antimonious sulphide, Sb_2S_3, and sulphur by the treatment with carbon disulphide.

[9] See page 356 for the removal of sulphur from sulphides and for an extraction apparatus.

[10] T. Paul, *Zeit. anal. Chem.*, **31**, 537, 1892. In fig. 87, *T* represents the thermometer, *B* a Habermann's wash-bottle containing sulphuric acid for cleaning the carbon dioxide. The carbon dioxide must be free from air, or some of the antimony will be oxidised to Sb_2O_4. F. Henz's gas generator (*Chem. Ztg.*, **26**, 386, 1902) is one of the best "CO_2 generators" for this experiment.

The sulphur in the precipitate is volatilised and the antimony pentasulphide is transformed into the grey trisulphide. The sulphur will all have volatilised in about an hour.[1] The crucible is cooled and weighed. When two successive weighings do not differ by more than 0·0005 grm., the operation is complete.
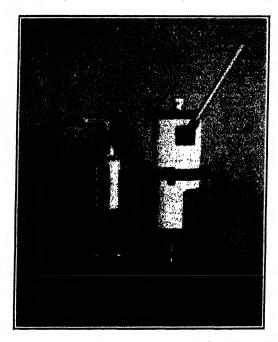
FIG. 87.—Ignition of Antimony Sulphide.

The weight of the precipitate—Sb_2S_3—multiplied by 0·8582 represents the corresponding amount of Sb_2O_3.

EXAMPLE.—The sulphide from 1 grm. of material, after half an hour's ignition in Paul's oven, as indicated above, gave, on first weighing, 0·02423 grm. Sb_2S_3. After ignition for another 15 minutes, the sulphide weighed 0·02418 grm. Hence 0·0242 × 0·8582 = 0·0208 grm., that is, 2·08 per cent. of Sb_2O_3.

The Accuracy of the Process.—One objection to this process is the great amount of oxalic and tartaric acid required to keep the tin in solution.[2] The chief errors arise from (1) the presence of free mineral acids; (2) the use of too concentrated solutions; (3) the error in assuming the ignited precipitate is normal trisulphide, Sb_2S_3; and (4) the presence of "fixed chlorine" (p. 296), introducing (a) an erroneous computation based on Sb_2S_3 when some SbSCl is present, and (b) the volatilisation of antimony chloride if the precipitate is melted. In illustration of the degree of accuracy which can be obtained with this method,

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[1] The heating should not extend much more than an hour, or some antimony sulphide may be lost by volatilisation, but, if chlorides are absent, the sulphide can be heated to its melting-point (540°–555°) in a current of carbon dioxide without loss. See L. A. Youtz, *Journ. Amer. Chem. Soc.*, 30, 975, 1908. According to A. Caffin (*Monit. Scient.*, (5), 4, 148, 1914), the determination of the sulphur in the antimony trisulphide checks the result.

[2] W. Dancer (*Journ. Soc. Chem. Ind.*, 16, 403, 1897) and J. Marburg (*Zeit. anal. Chem.*, 39, 47, 1900) first precipitate the tin with an excess of lime water.

the following numbers are cited for mixtures of known amounts of antimony and tin:—

Table XLII.—Test Analyses of Mixtures of Antimony and Tin.

Antimony.		Tin.	
Used.	Found.	Used.	Found.
0·0463	0·0462	0·2555	0·2532
0·0463	0·0461	0·1017	0·1011
0·0924	0·0923	0·0103	0·0103
0·1855	0·1853	0·1017	0·0999

If the antimony is to be separated from a complex enamel, naturally the values for the antimony will not be so concordant as this. The tin was here determined by the electrolytic process, page 320. The method thus gives good results, although it is somewhat laborious and consequently volumetric processes are used wherever practicable. The volumetric process, however, is not satisfactory when less than 1 per cent. of antimony is present. For many purposes the "iron precipitation" of antimony is the most convenient process for the separation of antimony from tin.[1]

Effect of Molybdenum.—The separation of arsenic and tin is even sharper than the separation of antimony and tin by Clarke's process. To separate molybdenum from "stannic" tin requires a modification of the process. Antimony and molybdenum are precipitated together. "By adding an alkali sulphide in excess to a solution containing a molybdate," says Clarke, "and then decomposing the thio-salt with a considerable quantity of dilute hydrochloric acid, and allowing the whole to stand overnight in a warm place, the molybdenum is precipitated. The sulphide thus obtained can be easily washed with a mixture of dilute hydrochloric acid and ammonium chloride. If now, by this process, we throw down tin and molybdenum together, every trace of the former metal may be dissolved out by boiling the mixed sulphides for about three-quarters of an hour with oxalic acid (20 grms. of oxalic acid per gram of tin). It is best to have present in the solution, while boiling, a little dilute hydrochloric acid. If antimony be present, it is necessary, just before ceasing to boil, to add to the solution an equal volume of a saturated solution of hydrogen sulphide to reprecipitate any antimony which may have gone into solution." [2]

§ 136. Herroun and Weller's Volumetric Iodide Process for Antimony.

The solution containing the antimony and tin may be divided into two parts: the antimony determined in one part by this or by Györy's process, and the tin in the other part by one of the processes indicated on page 316

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[1] For the "rapid" electro-deposition of both antimony and tin from the ammonium sulphide solution of the two sulphides, digestion of the mixed metals with aqua regia, and titration of the antimony by Herroun and Weller's process, see D. J. Demorest, *Journ. Ind. Eng. Chem.*, **2**, 80, 1910; *Chem. News*, **101**, 260, 1910.

[2] Tungsten gives discordant results. Sometimes the tungsten sulphide seems to dissolve like tin; at others, the solution is only partial—F. W. Clarke, *Amer. J. Science*, (2), **49**, 48, 1870; *Chem. News*, **21**, 124, 1870.

et seq. In Herroun and Weller's process[1] the antimony is all oxidised to antimony pentachloride, mixed with potassium iodide, and the amount of iodine liberated by the reduction of the antimonic to antimonious chloride determined by titration with sodium thiosulphate, as indicated on page 368, or by stannous chloride—the alternative process here described. Which process—thiosulphate or stannous chloride—is used will often be determined by the most convenient standard solutions.

The Oxidation of Antimonious to Antimonic Chloride.—The sulphide is transferred to a 600 c.c. Erlenmeyer's flask and dissolved by boiling with a mixture of concentrated hydrochloric acid and potassium chlorate. The latter is added in small portions at a time. The object is to convert the antimony trichloride— $SbCl_3$ —into the pentachloride— $SbCl_5$.[2] When the free chlorine and chlorine oxides have been driven off by boiling, and the volume of the solution is about 50 c.c., let the solution cool. When cold, add 20 c.c. of concentrated hydrochloric acid and dilute the solution to about 200 c.c. with cold, recently boiled distilled water.

The Liberation of Iodine.—Add, say, 5 grms. of potassium iodide dissolved in 10 c.c. of water. Stir the solution thoroughly. The antimony pentachloride is reduced to the trichloride. The reaction is represented:

$$SbCl_5 + 2KI \rightleftharpoons SbCl_3 + 2KCl + I_2$$

The solution now has a brown colour due to the liberated iodine. The strong acidity of the solution prevents the precipitation of antimony oxychloride. Dilute the solution to about 400 c.c.

Titration with Stannous Chloride.—Titrate the solution, at once,[3] with a standard solution of sodium thiosulphate or of stannous chloride.[4] The

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[1] E. F. Herroun, *Chem. News*, 45, 101, 1882; A. Weller, *Liebig's Ann.*, 213, 364, 1882; L. A. Youtz, *School Mines Quart.*, 24, 135, 407, 1903; *Zeit. anorg. Chem.*, 37, 337, 1903; A. Kolb and R. Formhals, *ib.*, 58, 202, 1908; E. Schmidt, *Chem. Ztg.*, 34, 453, 1910; H. Causse, *Compt. rend.*, 125, 1100, 1897; H. Giraud, *Bull. Soc. chim.*, (2), 46, 504, 1886; G. Rollin, *Ann. Chim. anal. app.*, 6, 114, 1902; G. von Knorre, *Zeit. angew. Chem.*, 1, 155, 1888; M. Rohmer, *Ber.*, 34, 1565, 1901; J. Darroch, *Chem. Eng.*, 4, 162, 1906; G. S. Jamieson, *Journ. Ind. Eng. Chem.*, 3, 250, 1911; F. Lehmann and M. Berdau, *Apoth. Ztg.*, 29, 186, 1914; F. Lehmann and B. Lokau, *Arch. Pharm.*, 252, 408, 1914; F. Utz, *Gummi-Zeit.*, 29, 137, 1914; P. E. Winkler, *Bull. Soc. chim. Belg.*, 36, 491, 1927; *Helv. Chim. Acta*, 10, 837, 1927.

[2] Any stannous salts which may be present are also oxidised to stannic salts.

[3] Iodine titrations are usually made in Erlenmeyer's flasks, not in beakers, on account of the volatility of the iodine during the titration. A large excess of potassium iodide lessens the danger of losing iodine in this way. For a similar reason, iodine titrations should be performed immediately the iodine has separated; and the solution should be cold. J. Wagner (*Zeit. anal. Chem.*, 27, 137, 1888; C. R. A. Wright, *Chem. News*, 21, 163, 1870) found that with the same amount of sodium thiosulphate solution:

Temperature	16°	30°	38°	50°	75°	83°	91°
Iodine sol.	39·6	39·8	40·0	40·1	40·7	40·9	41·4 c.c.

These numbers show that the higher the temperature, the less the amount of thiosulphate needed in titrating a given amount of iodine; and conversely. E. Sherer, *Chem. News*, 21, 141, 1870; A. Leclère, *Journ. Pharm. Chim.*, (7), 9, 341, 1914; W. T. Hall and J. Blatchford, *Chem. Met. Eng.*, 14, 164, 1916; J. T. Norton, *Amer. J. Sci.*, (4), 7, 287, 1899.

[4] STANDARD STANNOUS CHLORIDE.—Dissolve, say, 10 grms. of stannous chloride in 60 grms. of hydrochloric acid (sp. gr. 1·12). Dilute the solution to a litre. Dissolve 0·2 grm. of metallic antimony in concentrated hydrochloric acid and potassium chlorate (or bromine) in the cold. Metallic antimony is but slowly atacked by hot hydrochloric acid and potassium chlorate. Boil the solution to get rid of the chlorine oxides (or bromine). Cool and dilute. Add potassium iodide and carry out the titration as indicated in the text. The antimony equivalent of the standard solution of stannous chloride is thus simple arithmetic. Herroun and Weller titrated with standard sodium thiosulphate, but we prefer stannous chloride, if the preparation of the solution is not inconvenient. The objection to the stannous chloride

to arsenic.[1] A comparison of the two processes is interesting. The same general equation applies to both:

$$R_2O_3 + 2I_2 + 2H_2O \rightleftharpoons R_2O_5 + 4HI$$

Mohr→   ←Herroun and Weller

In Mohr's process, the reverse action indicated in the equation is prevented by keeping down the concentration of the hydriodic acid by means of an excess of alkali (sodium bicarbonate) in the solution. In Herroun and Weller's process, the reverse action is prevented by the relatively strong acidity of the solution.[2]

§ 137. Györy's Volumetric Bromate Process for Antimony.

This process [3] may be used as an alternative to that which precedes. Chemists who use this process regularly are enthusiastic about its merits. The sample under investigation is dissolved in a 250 c.c. Erlenmeyer's flask with 20 c.c. of concentrated hydrochloric acid and a little potassium chlorate or a few drops of bromine. Boil the solution.

Reduction of the Antimonic and Arsenic Salts.—Add, say, 0·75 grm. of crystalline sodium sulphite in order to reduce the antimonic to antimonious chloride and the arsenic to arsenious chloride.[4] Boil vigorously until the solution is reduced to about half its former volume. This drives off the sulphur dioxide and volatilises the arsenic.[5] Rinse the sides of the flask with hot water and add 10 c.c. of hydrochloric acid to the solution.

The Titration.—Heat the solution to about 80° or 90°, and titrate with a standard solution of potassium bromate [6] until nearly all the antimony is oxidised to antimonic chloride.[7] Add 3 drops of methyl orange, and continue the titration until the tint of the methyl orange is destroyed.[8] The solution

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[1] T. Smith, *Journ. Amer. Chem. Soc.*, 21, 769, 1899; F. A. Gooch and P. E. Browning, *Amer. J. Science*, (3), 40, 66, 1891; F. A. Gooch and J. C. Morris, *Zeit. anorg. Chem.*, 25, 227, 1900; *Amer. J. Science*, (4), 10, 151, 1900.

[2] A. Kolb and R. Formhals, *Zeit. anorg. Chem.*, 58, 189, 1908.

[3] S. Györy, *Zeit. anal. Chem.*, 32, 415, 1893; H. Nissenson and P. Siedler, *Chem. Ztg.*, 27, 749, 1903; E. Schmidt, *ib.*, 34, 453, 1910; J. B. Duncan, *Chem. News*, 95, 49, 1907; H. W. Rowell, *Journ. Soc. Chem. Ind.*, 25, 1181, 1906; F. Foerster, *Elektrochem. Zeit.*, 15, 232, 1909; A. Christensen, *Pharm. Ztg.*, 41, 326, 1896; W. Schmitz, *Gummi-Zeit.*, 28, 453, 1913; F. Utz, *ib.*, 29, 137, 1914; H. Nissenson, *Zeit. anorg. Chem.*, 81, 46, 1913; E. Zintl and H. Wattenburg, *Ber.*, 56, 472, 1923; O. Collenberg and G. Bakke, *Tids. Kemi Bergvæsen*, 3, 93, 104, 1923; J. Prescher, *Pharm. Zentralhalle*, 65, 61, 1924; T. Nakasono and S. Inoko, *Journ. Chem. Soc. Japan*, 47, 20, 1926; H. Heinrichs, *Glastech. Ber.*, 4, 130, 1927; L. R. W. McCay, *Journ. Amer. Chem. Soc.*, 50, 368, 1928; H. Blumenthal, *Zeit. anal. Chem.*, 74, 33, 1928; H. Biltz, *ib.*, 81, 82, 1930; C. W. Anderson, *Ind. Eng. Chem. Anal. Ed.*, 5, 32, 1933; 6, 456, 1934.

[4] The stannic chloride is not reduced.

[5] The amount of antimony "lost" by volatilisation or reoxidation is inappreciable. Most of the arsenic will be volatilised, since arsenious chloride is fairly volatile from boiling solutions. See page 269.

[6] POTASSIUM BROMATE SOLUTION.—Dissolve, say, 2·7836 grms. of the pure salt in a litre of water. To standardise the solution, dissolve 0·2 grm. of metallic antimony in hydrochloric acid and potassium chlorate as indicated on page 302, footnote 4. The reduction and titration of the resulting solution are conducted as indicated in the text.

[7] If lead be present, and the lead chloride separates as the solution cools, boil the solution again in order to keep the lead chloride in solution while the titration is in progress.

[8] Some prefer to use, as indicator, a solution of indigo made by dissolving powdered indigo in fuming sulphuric acid. Neutralise the solution with calcium carbonate; dilute with 10 times its volume of water and filter the blue liquid. Add 3 drops of this solution at the start and more when the reaction is nearly completed. The blue passes through various shades of greenish yellow into pale green. The colour is discharged with a drop of bromate in excess. The indigo solution is not so sensitive an indicator as the methyl orange and the results with the indigo are a little higher than with methyl orange.

should be thoroughly agitated during the titration, so that local excesses of bromate are not formed.[1] If very little bromate be needed, the indicator may be added before the titration. This, however, is an extreme case. If over 10 c.c. of bromate are needed, it is best to run in the greater part of the bromate before adding the indicator. The indicator has a tendency to fade, and if it be used from the start on an "unknown," it is necessary to add more from time to time as the titration progresses. The first titration may be used to find the approximate amount of bromate needed. The solution is run from the burette. The reaction is represented by the equation:

$$KBrO_3 + 7HCl + 3SbCl_3 = KCl + HBr + 3SbCl_5 + 3H_2O$$

Any further addition of bromate destroys the colour of the methyl orange, probably owing to the liberation of bromine by the action of free acid on the bromate, for if bromate be added after the methyl orange has lost its colour, the yellow colour of the bromine appears in a short time.

Influence of Foreign Substances.—The process works well in the presence of lead, zinc, tin,[2] silver, chromium and sulphuric acid, since these substances have no appreciable effect on the result. The presence of large amounts of calcium, magnesium and ammonium salts gives high results. Iron and copper are partly reduced by the sodium sulphite in the solution and hence react with the bromate, giving high results. Rowell states that 1 to 5 per cent. of iron raises the amount of antimony by approximately 0·02 per cent. He also states that, for every 0·1 per cent. of copper in the sample up to 1 per cent., 0·012 per cent. of antimony should be subtracted.

Accuracy of the Process.—The most important sources of error are: (1) incomplete expulsion of sulphur dioxide; (2) the imperfect volatilisation of arsenic, if present; and (3) over-titration, when too little hydrochloric acid is present, owing to the slowness of the reaction. In illustration of the accuracy of the process, the following determinations, by Rowell, may be quoted:—

Table XLIII.—Test Analyses of Antimony Ores.

| | Antimony (per cent.). | |
Nature of mixture.	Volumetric bromate process.	Gravimetric (as Sb_2S_3).
Antimony sulphide	71·40	71·35
Stibnite (As, Fe)	71·20	71·35
Lead : antimony	9·42	9·37
Lead : arsenic : antimony	8·65	8·70
Lead : antimony : tin	2·13	2·20

The analysis can thus be conducted with an accuracy approaching 0·05 of a unit in samples containing 10 per cent. of antimony. It may be a little difficult at first to get concordant results, but once the manipulation is mastered the process gives little trouble. J. B. Duncan states that "duplicates on a straight assay running 99·6 per cent. metallic antimony should agree exactly."

[1] Otherwise the results will be high owing to the loss of bromate before it attacks the antimony.
[2] Stannous salts are oxidised by the bromate, and F. Fichter and E. Müller (*Chem. Ztg.*, **37**, 309, 1913) use the reaction to determine tin.

The Influence of Arsenic.—The process indicated above can be used for the determination of arsenic,[1] but the solution cannot then be boiled in open vessels to expel the sulphur dioxide.   The boiling must be done in a flask fitted with a reflux condenser (fig. 88).   If the antimony is to be determined, and
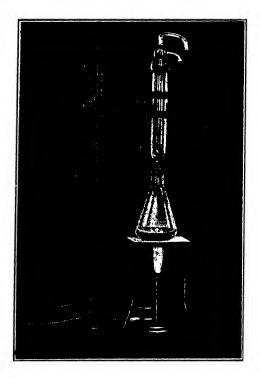
FIG. 88.—Reflux Condenser (see page 655).

arsenic is present in the sample, the latter must be removed, as indicated above, by boiling the solution down to half its volume in the presence of sodium sulphite.   If more than 2 or 3 per cent. of arsenic be present, add 20 c.c. more concentrated hydrochloric acid and 5 c.c. of a saturated aqueous solution of sulphur dioxide.   Boil the liquid down again.   There is no danger of an appreciable loss of antimony if the temperature be kept below 120°.   An artificial mixture of antimony and arsenic so treated gave 91·09 per cent. of antimony, when 90·91 per cent. was actually present.

Comparison Determinations.—To illustrate the results obtained in a separation of antimony and tin, the following duplicate determinations of the percentage amount of antimony with each of the processes here recommended, might be quoted:—

Henz and Clarke's process.	Herroun and Weller's process.	Györy's process.
26·96	26·33	26·52
26·10	26·23	26·59

[1] H. Biltz, *Zeit. anal. Chem.*, 81, 82, 1930; A. Schleicher and L. Toussaint, *Zeit. anorg. allgem. Chem.*, 159, 319, 1927.

§ 138. Low's Volumetric Permanganate Process for Antimony.

In this method, usually attributed to Low but anticipated many years previously by Kessler, antimony is titrated in sulphuric acid solution with standard potassium permanganate in the presence of excess of hydrochloric acid.[1] The reaction is symbolised:—

$$5Sb_2O_3 + 4KMnO_4 = 5Sb_2O_5 + 2K_2O + 4MnO$$

According to Pugh (l.c.), the determination of antimony by this method "becomes one of the simplest and most accurate of volumetric processes" provided the relative quantities of sulphuric and hydrochloric acids used are correctly adjusted. If too little hydrochloric acid is present, a basic antimony salt is precipitated, while too much causes reduction of the permanganate. Furthermore, in the absence of hydrochloric acid the reaction only follows the above course quantitatively under special conditions; otherwise the permanganate is partially reduced to trivalent manganese.

When titrating in the cold, Pugh recommends that the ratio of sulphuric to hydrochloric acid for a total volume of 200 c.c. shall be as follows:—

Conc. H_2SO_4, c.c.	.	.	.	0	10	20	30
Conc. HCl, c.c.	.	.	.	30–50	30–35	15–20	10–15

The solution containing the antimony is evaporated to strong fumes with, say, 20 c.c. of concentrated sulphuric acid.[2] After cooling, the solution is diluted somewhat [3] and boiled for 5 minutes to expel any sulphur dioxide. About 20 c.c. of concentrated hydrochloric acid are added, the solution diluted to 180 c.c., cooled to room temperature and then titrated with standard permanganate until the faint pink colour lasts for some 30 seconds.[4]

Errors.—Iron, if present, must be converted to the ferric state by oxidation with nitric acid and excess of the latter expelled by evaporation with sulphuric

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[1] F. Kessler, *Pogg. Ann.*, **118**, 17, 1863; O. Petriccioli and M. Reuter, *Zeit. angew. Chem.*, **14**, 1179, 1901; W. H. Low, *Journ. Amer. Chem. Soc.*, **29**, 66, 1907; E. Schmidt, *Chem. Ztg.*, **34**, 453, 1910; F. J. Mück, *ib.*, **46**, 790, 1922; A. Ecke, *ib.*, **48**, 537, 1924; J. H. Goodwin, *Journ. Ind. Eng. Chem.*, **3**, 42, 1911; D. J. Demorest, *ib.*, **5**, 842, 1913; C. R. McCabe, *ib.*, **9**, 42, 1917; L. I. Shaw, C. F. Whittemore and T. H. Westby, *ib.*, *Anal. Ed.*, **2**, 402, 1930; E. W. Hagmaier, *Met. Chem. Eng.*, **16**, 84, 1917; *Journ. Soc. Chem. Ind.*, **36**, 221, 1917; W. G. Leemann, *ib.*, **51**, 284T, 1932; L. Bertiaux, *Ann. Chim. anal.*, (1), **19**, 49, 1914; (2), **2**, 273, 1920; (2), **4**, 77, 1922; *Bull. Soc. chim.*, (4), **27**, 769, 1920; *Chim. et Ind.*, **4**, 467, 1920; O. Collenberg and G. Bakke, *Zeit. anal. Chem.*, **63**, 229, 1923; *Tids. Kemi Bergv.*, **3**, 93, 104, 1923; P. M. Koenig, *Chim. et Ind.*, *Special No.*, 125, May 1924; B. Paxton, *Chemist-Analyst*, **47**, 3, 1926; *Chem. Zentr.*, (2), 1672, 1926; W. W. Scott, *Standard Methods of Chemical Analysis*, New York, **1**, 28a, 28b, 1927; W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, New York, 228, 1929; J. E. Clennell, *Min. Mag.*, **45**, 151, 211, 1931; W. Pugh, *Journ. Chem. Soc.*, 1, 1933; L. R. W. McCay, *Journ. Amer. Chem. Soc.*, **50**, 368, 1928; H. H. Willard and P. Young, *ib.*, **50**, 1332, 1368, 1928; H. Rathsburg, *Ber.*, **61B**, 1663, 1928; J. Vorisek, *Chem. Listy*, **24**, 250, 1930; V. Auger, *Ann. Chim. anal. Chim. appl.*, **7**, 100, 1925; W. Manchot and F. Oberhauser, *Zeit. anorg. allgem. Chem.*, **139**, 40, 1924; K. Stanford and D. C. M. Adamson, *Analyst*, **62**, 23, 1937; R. G. Robinson, *ib.*, **62**, 191, 1937.

[2] Nitric acid, if present, must be expelled and organic matter destroyed. Ammonium persulphate can conveniently be used to oxidise organic matter, provided care is taken to reduce the solution before titration.

[3] If the treatment has been such as to oxidise the antimony up to the pentavalent state, the solution must be reduced at this stage by adding a slight excess of sodium sulphite and boiling off all sulphur dioxide. Iron, however, if present, will be wholly or partially reduced by this treatment—see under "Errors." For the direct titration of antimony in the pentavalent state by titanous chloride, see A. Oliverio, *Ann. Chim. applicata*, **21**, 211, 1931.

[4] A. Ecke (l.c.) and W. G. Leemann (l.c.) recommend the addition of Reinhardt's solution (page 501), when a much sharper end-point is obtained.

acid. The presence of lead leads to low results, as the precipitated lead sulphate occludes appreciable amounts of antimony sulphate. Pugh overcomes this difficulty by decanting off the clear solution from the precipitated lead sulphate. The precipitate is then dissolved in the appropriate volume of boiling concentrated hydrochloric acid and an equal volume of water. This solution is now added to the main solution and the whole titrated at 40° to 60°. The permanganate is added slowly to prevent its reduction by the hot hydrochloric acid. Towards the end-point a few drops of methyl orange are added and the titration continued until the colour of the indicator is discharged.

Trivalent arsenic interferes and should be removed. Vanadium, unless in the pentavalent state, must likewise be absent.

§ 139. The Volumetric Determination of Antimony and Arsenic in the Presence of Tin.

The arsenic and antimony in a solution containing antimony, arsenic and tin can be separately determined by the bromate process. The mixture is dissolved and oxidised as indicated for Györy's process. Make the solution up to, say, 200 c.c. Boil off the arsenic in an aliquot portion, say, 100 c.c., as indicated already, and titrate the solution for antimony with potassium bromate. The arsenic and antimony can be determined together in the other aliquot portion by proceeding as already indicated, but boiling down the solution using a reflux condenser (fig. 88). The difference in the two titrations represents the potassium bromate which is equivalent to the arsenic.[1]

EXAMPLE.—A solution was made up to 200 c.c. as indicated above. The antimony in 100 c.c. required 24·7 c.c. of a 0·1N-potassium bromate solution. This corresponds with $24·7 \times 0·00729 = 0·1801$ grm. of Sb_2O_3 in half the sample. The other portion, boiled under a reflux condenser, required 52·1 c.c. of the bromate solution. Hence $52·1 - 24·7 = 27·4$ c.c. of the bromate were required for the arsenic titration, corresponding to $27·4 \times 0·00495 = 0·1356$ grm. of As_2O_3 in half the sample.

§ 140. Metallic Precipitation.

In the ordinary zinc : carbon cell, if the metallic zinc be replaced successively by manganese, aluminium and magnesium, the voltage of the cell is increased; and conversely, if the zinc be similarly replaced by cadmium, iron and cobalt, the voltage is diminished. The order in which the metals can be thus arranged is the same as the order in which the metals displace one another in their salts. The order is approximately—

K, Na, Mg, Al, Mn, Zn, Cd, Fe, Co, Ni, Sn, Pb, Sb, Bi, As, Cu, Hg, Ag, Pt, Au

and the series is called the electrochemical series of the metals.[2] The order varies a little with different solutions and at different temperatures.[3] A metal on the left in the series will generally displace another metal on the right from its salt solution. Secondary reactions may prevent the actual precipitation of the

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[1] Rather more hydrochloric acid is required in the case of antimony than arsenic in order to prevent the precipitation of antimony during the titration, as a result of the increasing dilution of the solution. F. A. Stief, *Journ. Ind. Eng. Chem.*, **7**, 211, 1915.

[2] For metallic molybdenum and tungsten, see F. F. Smith, *Zeit. anorg. Chem.*, **1**, 360, 1892.

[3] G. M. Smith, *Journ. Amer. Chem. Soc.*, **27**, 540, 1905; J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, London, **1**, 1013, 1922.

metal. In many cases the displacement is so complete that the reaction can be used in quantitative analysis. What metals are precipitated often depends upon the acidity of the solution as well as on the metal used as precipitating agent.[1] In illustration of the more important metals used as precipitating agents, *magnesium* [2] precipitates zinc, cadmium, thallium, iron, cobalt, nickel, tin, lead,[3] antimony,[4] bismuth, copper,[5] mercury, silver,[6] platinum and gold. Some part of the antimony may be evolved as a gas when solutions containing antimony are treated with magnesium or zinc; and arsenic is also lost in this way when its solutions are treated with zinc, magnesium and iron.[7] *Aluminium* precipitates lead,[8] antimony,[9] tin, copper, tellurium,[10] silver.[11] *Zinc* precipitates cadmium, cobalt, nickel,[12] tin, lead,[13] antimony,[14] bismuth, arsenic, copper,[15] mercury, silver, palladium, rhodium, iridium, osmium, platinum, gold, but not iron.[16] Zinc also reduces the salts of iron, manganese, titanium, tungsten, molybdenum, chromium and vanadium to a lower state of oxidation. *Cadmium* precipitates copper, lead, silver,[17] antimony, tin. *Iron* precipitates bismuth,[18] antimony,[19] copper, mercury, silver, lead, gold. In the presence of stannic chloride, arsenic is also precipitated. Metallic iron also reduces ferric to ferrous salts, stannic to stannous salts.[20] *Tin* precipitates antimony, arsenic,

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[1] J. B. Senderens, *Bull. Soc. chim.*, (3), 11, 424, 1163, 1894; *ib.*, (3), 15, 208, 691, 1896; *ib.*, (3), 17, 271, 1897; D. Tommasi. *ib.*, (3), 17, 440, 1897.

[2] For the action of magnesium on manganese salts, see J. G. Hibbs and E. F. Smith, *Journ. Amer. Chem. Soc.*, 16, 822, 1894; *Chem. News*, 71, 2, 1895; G. A. Maack, *Untersuchungen über das Verhalten des Magnesiums und Aluminiums gegen Salzlösungen verschiedener Metalle*, Göttingen, 1862; T. L. Phipson, *Jahrb.*, 192, 1864; Z. Roussin, *ib.*, 170, 1866; A. Commaille, *Compt. rend.*, 63, 556, 1866; S. Kern, *Chem. News*, 33, 236, 1876; C. Pertusi, *Ann. Chim. anal.*, 20, 229, 1915.

[3] W. Schulte, *Metallurgie*, 6, 214, 1909.

[4] S. Kern, *Chem. News*, 32, 309, 1875; E. G. Bryant, *ib.*, 79, 75, 1899.

[5] A. Villiers and F. Borg, *Bull. Soc. chim.*, (3), 9, 602, 1893; *Chem. News*, 68, 263, 1893.

[6] E. G. Bryant, *Chem. News*, 79, 75, 1899.

[7] Z. Roussin, *Journ. Pharm. Chim.*, (4), 3, 413, 1866; *Chem. News*, 14, 27, 1866. W. N. Hartley, *ib.*, 14, 73, 1866 (failed to precipitate iron with magnesium); S. Kern, *ib.*, 33, 236, 1876; T. L. Phipson, *ib.*, 9, 219, 1864; A. Commaille, *Compt. rend.*, 63, 556, 1866; F. Clowes and R. M. Caven, *Chem. News*, 76, 297, 1897; E. G. Bryant, *ib.*, 79, 75, 1899. J. G. Hicks and E. F. Smith (*Journ. Amer. Chem. Soc.*, 16, 822, 1894) have studied the action of magnesium on manganous salts.

[8] A. H. Low, *Journ. Anal. App. Chem.*, 4, 12, 1891; 6, 664, 1892; J. E. Williams, *Eng. Min. Journ.*, 53, 641, 1892.

[9] W. Schulte, *Metallurgie*, 6, 214, 1909.

[10] G. A. Maack, *Untersuchungen über das Verhalten des Magnesiums und Aluminiums gegen Salzlösungen verschiedener Metalle*, Göttingen, 1862.

[11] N. Tarugi, *Gazz. Chim. Ital.*, 33, ii, 223, 1903.

[12] J. L. Davies, *Journ. Chem. Soc.*, 28, 311, 1875.

[13] F. Stolba (*Journ. prakt. Chem.*, (1), 101, 150, 1867; *Chem. News*, 17, 2, 1868) precipitates lead from lead salts quantitatively by metallic zinc in the presence of hydrochloric acid on a water bath. L. T. Merrill, *Eng. Min. Journ.*, 91, 56, 1911; A. Eckenroth, *Pharm. Ztg.*, 40, 528, 1895; F. Mohr, *Zeit. anal. Chem.*, 12, 142, 1873; C. Rössler, *ib.*, 24, 1, 1885.

[14] A. Ditte and R. Metzner, *Compt. rend.*, 117, 691, 1893.

[15] J. C. Shengel and E. F. Smith, *Journ. Amer. Chem. Soc.*, 21, 932, 1899; *Chem. News*, 81, 134, 1900; M. Cottereau, *Compt. rend.*, 22, 1146, 1846) separated copper from tin by taking advantage of the fact that when zinc is placed in a solution of the mixed chlorides, the copper precipitates before the tin.

[16] M. Demarçay, *Bull. Soc. chim.*, (2), 32, 610, 1879; see also page 170.

[17] A. W. Classen, *Journ. prakt. Chem.*, (1), 97, 217, 1866; *Chem. News*, 13, 232, 1866.

[18] J. Clark (*Journ. Soc. Chem. Ind.*, 19, 26, 1900) for the separation of bismuth and lead. J. C. Galletly and G. G. Henderson (*Analyst*, 34, 389, 1909) recommend the process using a hot solution containing 2·5 per cent. of free nitric acid.

[19] A. Thiel and K. Keller, *Zeit. anorg. Chem.*, 68, 42, 1910.

[20] Iron also precipitates tin from solutions of stannous salts which are neither too dilute nor too acid. A. Thiel and K. Keller, *Zeit. anorg. Chem.*, 68, 220, 1910.

copper, mercury, silver, gold, lead.[1] *Copper* precipitates mercury, silver, gold, but not tin; *lead* precipitates bismuth,[2] tin.[3]

Precipitation of Antimony in the Presence of Tin—Tookey's Process.—The separation of antimony from tin by precipitation of the antimony, as metal, from a hot hydrochloric acid solution by means of metallic iron [4] was proposed by Tookey in 1862.[5] The process can be conducted in the following manner :— Dissolve the mixed sulphides in a warm mixture of hydrochloric acid and potassium chlorate and boil off the chlorine. The solution should contain about 12 per cent., and in any case not less than 2 per cent., of the acid, or some tin may be precipitated. Place some coarse granules of pure [6] metallic iron in the solution very nearly at the boiling temperature. Add more hydrochloric acid as the iron dissolves. When all the antimony is precipitated,[7] filter the solution as quickly as possible, since some antimony may redissolve when the solution is exposed to the air. An excess of iron is necessary and the precipitated antimony must be mixed with the iron during the filtration.[8] The mixture of metallic antimony and iron can then be dissolved in a mixture of hydrochloric acid and potassium chlorate, and the antimony determined by precipitation as sulphide.

Working with known mixtures of stannic chloride and antimony trichloride, Hoffmann found the following results :—

Antimony'	.	.	0·1	0·2	0·4	0·1	0·2	0·4	grm.
Tin used .	.	.	0·4343	0·4343	0·4343	0·8686	0·8686	0·8686	grm.
Tin found	.	.	0·4336	0·4337	0·4338	0·8684	0·8687	0·8685	grm.
Error	.	.	− 0·0007	− 0·0006	− 0·0005	− 0·0002	+ 0·0001	− 0·0001	grm.

The results are therefore quite satisfactory.[9]

§ 141. The Electro-deposition of Antimony.

Two distinct types of processes have been used for the electro-deposition of antimony. In the earlier developed methods, the antimony is separated as

[1] O. Sackur, *Arb. Kais. Ges.-A.*, 20, 512, 1904.

[2] C. Ullgren (*Berzelius' Jahrb.*, 21, 148, 1842) and A. Patera (*Zeit. anal. Chem.*, 5, 226, 1866) separate bismuth from lead in this way; but according to O. Steen (*Zeit. angew. Chem.*, 8, 531, 1895) the error lies between 20 and 30 per cent.

[3] O. Sackur, *loc. cit.*

[4] J. L. Gay-Lussac (*Ann. Chim. Phys.*, (2), 46, 222, 1831; J. H. Mengin, *Compt. rend.*, 119, 224, 1894; *Chem. News*, 70, 93, 1894) precipitated antimony in the presence of tin by means of metallic tin in hydrochloric acid solution. If zinc is used instead of iron, some antimony may be lost as hydride. No antimony is lost as hydride when iron is used— M. Dupasquier, *Compt. rend.*, 14, 514, 1842.

[5] C. Tookey, *Journ. Chem. Soc.*, 15, 462, 1862; J. Attfield, *Pharm. Journ.*, (2), 10, 512, 1870; A. W. Classen, *Journ. prakt. Chem.*, (1), 92, 477, 1864; *Chem. News*, 13, 232, 1866; O. Low, *Vierteljahr. prakt. Chem.*, 14, 406, 1864; A. Carnot, *Compt. rend.*, 114, 587, 1892; J. H. Mengin, *ib.*, 119, 224, 1894; M. Hoffmann, *Beiträge zur Kenntnis der analytischen Chemie des Zinns, Antimons, und Arsens*, Berlin, 27, 1911; P. Wenger and G. Paraud, *Ann. Chim. anal. Chim. appl.*, 5, 230, 1923.

[6] C. Rammelsberg recommends iron reduced in hydrogen gas. Bright piano wire will do quite well.

[7] If the volume of the solution is small this will take about 20 minutes.

[8] A. W. Classen (*l.c.*) has shown that the precipitated antimony is perceptibly soluble in hot or cold hydrochloric acid of various strengths and hence antimony may be lost. By following the plan described in the text, this loss is made negligibly small.

[9] The tin was determined in the filtrate, after the separation of the antimony, by precipitation as sulphide. G. Panajotow (*Ber.*, 42, 1296, 1909) separates antimony from tin by precipitating the antimony as sulphide from a solution containing 15 per cent. of HCl, at ordinary temperatures. The tin remains in solution. The results seem to be good—A. Inhelder, *Beitrag zur Trennung des Antimons und Zinns und zur Analyse von Lagermetallen*, Zürich, 1911. See also footnote 5, page 273.

sulphide. The sulphide is dissolved in aqueous sodium sulphide and the resulting solution is then electrolysed. As, however, polysulphides must be absent, a suitable reducing agent, usually potassium cyanide, is added to the bath to destroy them, if and when formed:—

$$Na_2S_x + (x-1)KCN = Na_2S + (x-1)KCNS \,[1]$$

Smith recommends the following procedure. To the solution of antimony as chloride are added 15 c.c. of sodium sulphide solution (sp. gr. 1·18), 3 grms. of potassium cyanide and 1 c.c. of 10 per cent. sodium hydroxide solution. After dilution with water to 70 c.c., the solution is heated nearly to boiling and electrolysed with a current density of 6 amperes per 100 sq. cm. at 3·5 to 4 volts. A rotating anode, making 400 to 500 revolutions per minute, is used. Up to 1 grm. of metal can be deposited in a compact form on sand-blasted platinum dishes in less than half an hour.

Electro-deposition from a sulphide bath is said to give high results, which have been attributed in turn to (1) oxidation of the deposited metal during and through electrolysis, together with occlusion of sulphur compounds in the deposit;[2] (2) to the presence of antimony hydride in the separated metal;[3] and (3) to the occlusion of mother liquor in the pits when a platinum basin with a roughened inner surface is used as the cathode.[4] Conversely, it has been stated that the results are apt to be low owing to some of the metal passing to the anode in the form of a complex ion.[5]

In the more recent methods, the antimony is deposited from, usually, a solution of its chloride in hydrochloric acid in the presence of a hydrazine or hydroxylamine salt to reduce the evolved chlorine.[6]

Schleichner suggests that Engelberg's modification of Classen's process should be adopted as a standard procedure.

[1] F. Wrightson, *Zeit. anal. Chem.*, **15**, 297, 1876; C. Luckow, *ib.*, **19**, 1, 1880; J. P. Cooke, *Proc. Amer. Acad.*, **13**, 1, 1878; **15**, 251, 1880; G. Parodi and A. Mascazzini, *Zeit. anal. Chem.*, **18**, 587, 1879; A. Classen and M. A. von Reis, *Ber.*, **14**, 1622, 1881; A. Classen, *ib.*, **17**, 2467, 1884; A. Classen and R. Ludwig, *ib.*, **18**, 1104, 1885; **19**, 323, 1886; A. Lecrenier, *Chem. Ztg.*, **13**, 1219, 1890; G. Vortmann, *Ber.*, **24**, 2749, 1891; F. Rüdorff, *Zeit. angew. Chem.*, **5**, 197, 1892; A. Ditte and R. Metzner, *Ann. Chim. Phys.*, (6), **29**, 389, 1893; A. Classen, *Ber.*, **27**, 2060, 1894; H. Ost and W. Klapproth, *Zeit. angew. Chem.*, **13**, 827, 1900; H. Danneel and H. Nissenson, *Inter. Cong. angew. Chem.*, **4**, 678, 1903; F. F. Exner, *Journ. Amer. Chem. Soc.*, **25**, 896, 1903; A. Hollard, *Bull. Soc. chim.*, (3), **29**, 262, 1903; *Chem. News*, **87**, 282, 1903; F. Henz, *Zeit. anorg. Chem.*, **37**, 1, 1903; A. Fischer, *Ber.*, **36**, 2348, 3345, 1903; *Zeit. anorg. Chem.*, **42**, 363, 1904; A. Fischer and R. J. Boddaert, *Elektrochem. Zeit.*, **10**, 945, 1904; H. D. Law and F. M. Perkin, *Trans. Faraday Soc.*, **1**, 262, 1905; A. Hollard and L. Bertiaux, *Bull. Soc. chim.*, (3), **31**, 900, 1904; J. A. Langness and E. F. Smith, *Journ. Amer. Chem. Soc.*, **27**, 1524, 1905; J. M. M. Dormaar, *Zeit. anorg. Chem.*, **53**, 349, 1907; *Chem. Weekblad*, **4**, 55, 1907; F. Foerster and J. Wolf, *Elektrochem. Zeit.*, **13**, 205, 1907; E. Cohen, *ib.*, **14**, 301, 1908; O. Scheen, *ib.*, **14**, 257, 1908; F. Utz, *Gummi-Ztg.*, **28**, 126, 1913; A. Caffin, *Monit. Scient.*, (5), **4**, 148, 1914; N. K. Chaney, *Journ. Amer. Chem. Soc.*, **35**, 1482, 1913.

[2] *Loc. cit.*, F. Henz; J. M. M. Dormaar; F. Foerster and J. Wolf.

[3] *Loc. cit.*, C. Luckow; A. Caffin.

[4] *Loc. cit.*, O. Scheen.

[5] *Loc. cit.*, A. Fischer and R. J. Boddaert.

[6] H. J. S. Sand, *Elektrochem. Zeit.*, **13**, 326, 1907; *Journ. Chem. Soc.*, **93**, 1572, 1908; E. P. Schoch and D. J. Brown, *Eighth Inter. Cong. App. Chem.*, **21**, 81, 1912; *Journ. Amer. Chem. Soc.*, **38**, 1660, 1916; A. J. Engelberg, *Zeit. anal. Chem.*, **62**, 257, 1923; A. Lassieur, *Compt. rend.*, **177**, 263, 1923; **179**, 632, 827, 1924; *Ann. Chim.*, **3**, 269, 1924; *Bull. Soc. chim.*, **39**, 1167, 1926; A. Schleichner and L. Toussaint, *Chem. Ztg.*, **49**, 645, 1925; A. Schleichner, *Zeit. anal. Chem.*, **69**, 39, 1926; J. Lukas and A. Jílek, *Chem. Listy*, **20**, 63, 130, 170, 1926; D. J. Brown, *Journ. Amer. Chem. Soc.*, **48**, 582, 1926; A. Schleichner and L. Toussaint, *Zeit. anorg. allgem. Chem.*, **159**, 319, 1927; H. Hölemann, *Zeit. anal. Chem.*, **81**, 161, 1930.

The details for the process are as follows. The antimony salt, containing not more than 0·5 grm. of antimony, is dissolved in 10 c.c. of concentrated hydrochloric acid,[1] 2 grms. of hydroxylamine hydrochloride, $NH_2OH.HCl$, are added and the solution diluted to 200 c.c. The electrolysis is carried out at 60° to 70°, keeping the cathode potential between 0·28 and 0·35 volt against a calomel cell and with a current of 1 to 0·5 ampere. Gauze electrodes, rotating at 800 to 1000 revolutions per minute, are used.

§ 142. The Evaluation of Antimony Compounds.

Antimony oxide may be evaluated by a method similar to that used for arsenious oxide (page 294). Add, say, 0·1 grm. of antimonious oxide to 20 c.c. of water; heat the liquid to boiling; add tartaric acid in small quantities at a time until the oxide is completely dissolved.[2] Neutralise the solution with sodium bicarbonate and add 10 c.c. more of the sodium bicarbonate solution. Titrate with iodine using starch as indicator as described for Mohr's process for arsenic, page 290.[3] Since $Sb_2O_3 + 2H_2O + 2I_2 = 4HI + Sb_2O_5$, every gram of iodine represents 0·5742 grm. of Sb_2O_3. Antimonic compounds are reduced [4] as indicated under Györy's process, and determined by Mohr's or by Györy's process.[5]

[1] A. Schleichner and L. Toussaint (v. supra) neutralise with sodium hydroxide until a faint precipitate forms and then redissolve it in hydrochloric acid. They state that, if excess hydrochloric acid is present, the deposited antimony will contain antimony chloride.

[2] The tartaric acid keeps the antimony oxide in solution—F. H. Alcock, *Pharm. Journ.*, 362, 1900.

[3] Titrate at once, or antimonious hydroxide may be precipitated.

[4] B. S. Evans (*Analyst*, 56, 171, 1931) reduces with sodium hypophosphite, $NaH_2PO_2.H_2O$.

[5] R. Rickmann (*Zeit. angew. Chem.*, 25, 1518, 1912) detects antimony in enamels by cleaning the enamel free from adhering iron, and then boiling the powdered enamel with a 4 per cent. solution of acetic acid (or 2 per cent. tartaric acid). Divide the solution into two parts. Test one part with hydrogen sulphide, and titrate the other part with standard permanganate. If antimony is present, and no permanganate is consumed, it is inferred that the enamel contains a metantimonate which Rickmann says is harmless. O. Collenberg and G. Bakke, *Tids. Kemi Bergv.*, 3, 93, 104, 1923.

CHAPTER XXIII.

THE DETERMINATION OF TIN.

§ 143. The Detection of Tin.

CLARK has shown that 4-methyl-1 : 2-dimercaptobenzene and 4-chloro-1 : 2-dimercaptobenzene are specific reagents for tin.[1] The test is carried out by adding a few drops of a 0·2 per cent. solution of either reagent in sodium hydroxide solution to the suspected solution, acidified with up to 15 per cent. of hydrochloric acid. On warming, a pink to magenta-red colour develops within a few seconds if as little as one part in a million of stannous tin is present. If the tin is in the stannic state, the colour develops more slowly and the test is not so sensitive. Consequently a trace of thioglycollic acid should be added before applying the test to ensure that the tin is in the stannous condition. No other elements interfere except bismuth, which gives a brick-red precipitate quite unlike the colour given by tin. The test has been adapted for the colorimetric determination of tin and has been found to give an accuracy of about 10 per cent. with from 1 to 5 parts of tin per million of solution.

§ 144. The Metallic Precipitation of Tin.

Tin may be conveniently precipitated in the metallic state by means of metallic zinc, aluminium or cadmium. This reaction also offers a convenient method of separating tin in the filtrate from the antimony sulphide obtained in Clarke and Henz's process (page 298).[2] Boil off the hydrogen sulphide.

Precipitation of Metallic Tin.—Place a piece of zinc [3] (foil, ribbon or stick) in the solution and heat the solution nearly to the boiling-point over a small flame. In about 20 minutes, test a few drops of the clear liquid for tin by means of a solution of hydrogen sulphide. If necessary, heat the solution a little longer until all the tin is precipitated. Decant the liquid through a small filter-paper and transfer the metallic tin and zinc to the filter-paper. Wash with water.

Conversion of the Metallic Tin into Stannic Oxide.—Rinse the metallic tin and zinc into a 250 c.c. beaker. The total volume of the liquid will be about 10 c.c. Add 10 c.c. of nitric acid and cover the beaker with a clock-glass.[4] When all the zinc is dissolved, and the tin oxidised, dilute the solution to 40–50

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[1] R. E. D. Clark, *Analyst*, **61**, 242, 1936. For the preparation of the reagents, see W. H. Mills and R. E. D. Clark, *Journ. Chem. Soc.*, 175, 1936; R. E. D. Clark, *Tech. Publ. Internat. Tin Res. Dev. Council*, A, No. 41, 1936. For the detection of tin by nitrophenylarsinic acid, see B. Tougarinoff, *Bull. Soc. chim. Belg.*, **45**, 542, 1936.

[2] C. Ratner, *Chem. Ztg.*, **26**, 873, 1902; G. Buchner, *ib.*, **18**, 1904, 1894; L. Vignon, *Compt. rend.*, **107**, 734, 1888.

[3] Free from tin. For lead in place of zinc, see A. Pleischl, *Dingler's Journ.*, **164**, 200, 1862. For precipitation by magnesium, see C. Pertusi, *Ann. Chim. anal.*, **20**, 229, 1915.

[4] If the reaction be too violent, dilute the solution with cold water. If the action ceases, warm the solution.

c.c. Carefully heat the solution to boiling and stir vigorously. Let settle. Add 5 grms. of ammonium nitrate; filter and wash with a 5 per cent. solution of ammonium nitrate. Burn the filter-paper in a crucible. Moisten the ash with nitric acid; dry on a water bath; ignite the precipitate, gently at first, and finally over a blast.[1] Weigh the precipitate as SnO_2.

Tin and antimony can be together precipitated by cadmium and weighed. By digesting the mixed metals in hydrochloric acid, the tin dissolves, and antimony remains behind. The antimony can be washed, dried and weighed. The amount of tin is obtained by difference.[2] Stannic salts are reduced to stannous salts by metallic iron, but no tin is precipitated.

§ 145. The Precipitation of Tin as Hydroxide—Löwenthal's Process.

There are two stannic oxides corresponding with SnO_2. The one is called α-stannic acid, or α-metastannic acid; the other, β-stannic acid, or β-metastannic acid.[3] α-Stannic acid dissolves quickly in cold dilute mineral acids —nitric, hydrochloric and sulphuric acids. The solution, on prolonged boiling, deposits the β-acid, which is practically insoluble in dilute acids.[4] Salts corresponding with the two stannic acids are known.

In Löwenthal's process [5] for the determination of tin, ammonia is added to the solution containing stannic chloride [6] until a permanent precipitate just begins to form. Add dilute hydrochloric acid, drop by drop, with constant stirring, until the precipitate is all just redissolved. Add a cold saturated solution of ammonium nitrate [7] to the solution and boil for some time.[8] When all the tin is precipitated, let the precipitate settle and wash by decantation with a 5 per cent. solution of ammonium nitrate until the precipitate is free from chlorides.[9] After burning the filter-paper, moisten the ash with nitric acid, evaporate to dryness on a water bath, add the precipitate and ignite at a gradually rising temperature. Finish the ignition on a blast [10]; weigh as stannic oxide—SnO_2.

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[1] If traces of chlorides are present, some tin may be lost by volatilisation as chloride. In fact, it is sometimes convenient to remove tin from a precipitate by mixing it with ammonium chloride and calcining the mixture—H. Rose, *Pogg. Ann.*, 112, 163, 1861.

[2] J. H. Mengin, *Compt. rend.*, 119, 224, 1894; J. L. Gay-Lussac, *Ann. Chim. Phys.*, (2), 46, 222, 1831.

[3] J. J. Berzelius, *Ann. Chim. Phys.*, (1), 87, 50, 1813; R. Engel, *Compt. rend.*, 124, 766, 1897; 125, 464, 651, 709, 1897; C. F. Barfoed, *Zeit. anal. Chem.*, 7, 260, 1868; J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, London, 7, 404, 1927.

[4] D. B. Dott, *Pharm. Journ.*, (4), 27, 486, 1908.

[5] J. Löwenthal, *Journ. prakt. Chem.*, (1), 56, 366, 1852.

[6] If stannous chloride be present, oxidise with bromine or chlorine water.

[7] Or sodium sulphate. H. Rose (*Pogg. Ann.*, 112, 164, 1861; *Chem. News*, 5, 87, 1862) used sulphuric acid for the precipitation.

[8] To make sure all the tin is precipitated, add a few drops of the clear solution to a hot solution of ammonium nitrate or sodium sulphate. If all the tin is precipitated, no further precipitation will occur.

[9] If washed with boiling water, a turbid filtrate may be produced. R. Bunsen's plan (*Liebig's Ann.*, 106, 13, 1858) of washing with ammonium acetate or ammonium nitrate removes this difficulty. For the colloidal stannic acids, see J. M. van Bemmelen, *Zeit. anorg. Chem.*, 23, 124, 1900. M. Liebschutz (*Chem. News*, 102, 213, 1910; *Chemist-Analyst*, 9, 5, 1914) adds a dilute solution of albumen (egg-white) to the solution from which the colloidal metastannic acid is to be precipitated, and heats the solution for a short time. The stannic acid is entangled with the albumen as the latter curdles. The curd is filtered at once. Any copper, etc., entangled with the tin is removed by boiling the precipitate with dilute nitric acid. The method is also recommended for the sulphides of zinc, lead, etc. Paper pulp acts well with this and similar precipitates. See also pages 85 and 160.

[10] Mere heating to redness does not suffice to expel all the water—J. B. Dumas, *Liebig's Ann.*, 105, 104, 1858.

Tin is sometimes separated from its solutions by evaporating the solution to dryness with nitric acid. The tin is thus converted into the insoluble metastannic acid, which is converted by ignition into stannic oxide.[1]

Errors.—There are several objections to this process. The great difficulty is involved in washing the precipitate. If iron be present in the solution the precipitate, after washing, is almost sure to be contaminated with appreciable quantities of iron oxide.[2] Other oxides may also contaminate the precipitate. Antimony hydroxide, for example, may be nearly all precipitated with the tin. Hoffmann[3] thinks that an insoluble tin antimonate—$3SnO_2.2SbO_2$—is formed. Arsenic also is precipitated, probably as tin arsenate[4]—$2SnO_2.As_2O_5$—a reaction which Hoffmann has suggested for the gravimetric determination of arsenic. Reynoso's process for the determination of phosphoric acid, and also of tin, is based on the insolubility of tin phosphate in nitric acid; iron also may form a sparingly soluble metastannate or a ferric phosphostannate.[5] Lepéz and Storch (*l.c.*) have shown that bismuth too, if present in considerable quantities, will contaminate the precipitated stannic oxide.

Hence, in a general way, *avoid the determination of tin by separating the tin as stannic acid*, since the stannic oxide may be contaminated with, *inter alia*, silica, phosphates, arsenates, antimonates, lead, bismuth and ferric oxides.

§ 146. The Precipitation of Tin as Sulphide.

The precipitation of tin by metallic zinc is much easier than the usual process of separation by precipitation as sulphide or hydroxide and weighing as stannic oxide. Whenever convenient, analysts avoid the precipitation of tin both as sulphide and hydroxide (stannic acid).

Precipitation of Tin Sulphide.—The combined filtrates containing the tin are neutralised with ammonia, acidified with acetic acid and saturated with hydrogen sulphide. The stannic sulphide is but very slightly soluble in acetic acid solution.[6] Let the precipitate stand in a warm place over-night.[7] Decant

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[1] C. Bunge, *Pharm. Zentr.-h.*, 54, 845, 1913.

[2] According to H. Rose (*Pogg. Ann.*, 112, 169, 1861), the iron becomes soluble when the solution is evaporated to dryness. C. Lepéz and L. Storch (*Monats.*, 10, 283, 1889) show that iron, chromium and cerium lead to the incomplete precipitation of metastannic acid in dilute nitric acid solutions; while aluminium, uranium, cobalt, nickel and copper do not. F. H. van Leent (*Monit. Scient.*, (4), 12, 866, 1899; *Chem. News*, 78, 320, 1898) states that chromium and aluminium, as well as iron, retard the precipitation of metastannic acid. R. E. Lee, J. P. Trickey and W. H. Fegely, *Journ. Ind. Eng. Chem.*, 6, 536, 1914.

[3] M. Hoffmann, *Beiträge zur Kenntnis der analytischen Chemie des Zinns, Antimons, und Arsens*, Berlin, 45, 1910.

[4] E. Haeffely, *Phil. Mag.*, (4), 10, 220, 1855.

[5] U. Antony and G. Hajon-Mondolfo, *Gazz. Chim. Ital.*, 27, ii, 142, 1898; A. Reynoso, *Compt. rend.*, 33, 385, 1851; *Journ. prakt. Chem.*, (1), 54, 261, 1851.

[6] If Clarke and Henz's process has been used, the solution contains ammonium oxalate and tartrate. These exert an appreciable solvent action on the tin sulphide—another reason for condemning the gravimetric process. Clarke (page 195) destroyed the organic acids by means of potassium permanganate before precipitating the tin as sulphide. G. W. Wdowiszewski (*Stahl Eisen*, 27, 781, 1907) destroys organic matter (tartaric acid) by digesting the solution in a covered beaker with 50 c.c. nitric acid (sp. gr. 1·4) and 10 c.c. of sulphuric acid (sp. gr. 1·65). The solution is evaporated on a sand bath down to about 30 c.c. The black or brown mass becomes almost colourless when mixed with 20 c.c. nitric acid. In the case of tin, of course, stannic oxide would be precipitated by this treatment. See also W. R. Schoeller, *Analyst*, 56, 306, 1931.

[7] The tin sulphide is a difficult precipitate to deal with, because it separates in a slimy condition, especially if the solution be boiled during the passage of the gas. The slimy precipitate also retains alkali salts very tenaciously and is difficult to wash, particularly in the absence of ammonium salts. See page 85.

the clear liquid through a Gooch crucible and wash the precipitate four or five times by decantation with a solution of ammonium nitrate or acetate.[1] Finally transfer the precipitate to the crucible and wash free from chlorides.

Conversion of Sulphide into Oxide.[2]—Dry the Gooch crucible and heat the crucible very gently in its saucer with free access of air until the smell of sulphur dioxide is no longer perceptible. If the temperature be raised too rapidly, at this stage fumes of stannic sulphide would be evolved and burnt to stannic oxide, consequently giving low results.[3] The crucible should be covered with a lid to prevent loss by decrepitation during the earlier stages of the ignition. Remove the lid and raise the temperature gradually with free access of air. Finish off by blasting the crucible for half an hour. Cool the crucible in a desiccator.

Removal of Sulphates.—The stannic oxide—SnO_2—so formed holds a little sulphuric acid[4] very tenaciously. Hence, weigh the crucible, place a piece of ammonium carbonate—about half a centimetre diameter—in the crucible, and blast it again. This treatment with the ammonium carbonate is repeated until two successive weighings do not differ by more than 0·0005 grm.[5]

The result is generally a little too high because of the adsorption of alkalies and the difficulty which attends the complete conversion of tin sulphide to tin oxide. A little sulphate also is nearly always retained by the oxide. As a consequence of these facts, *the gravimetric determination of tin as sulphide is used as little as possible.*[6] Electrolytic or volumetric processes are far more satisfactory.

§ 147. The Volumetric Determination of Tin—Mène's Ferric Chloride Process.

This method is founded upon the fact that tin sulphide can be dissolved in hydrochloric acid and the resulting stannic chloride reduced to stannous chloride by means of an excess of metallic iron.[7] The solution of stannous chloride is then titrated with a standard ferric chloride solution,[8] which oxidises the stannous chloride back to stannic chloride: $SnCl_2 + 2FeCl_3 = SnCl_4 + 2FeCl_2$.[9]

Precipitation of the Tin.—If other metals are present, the strongly acid solution is reduced by warming it at 80° or 90° with a piece of iron wire, when mercury, arsenic, antimony, copper and bismuth, if present, are precipitated.

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[1] R. Bunsen, *Liebig's Ann.*, **106**, 13, 1858. For the solubility of stannic sulphide in ammonium carbonate solution, see F. W. Schmidt, *Ber.*, **27**, 2739, 1894.

[2] J. Löwenthal, *Journ. prakt. Chem.*, (1), **56**, 366, 1852.

[3] For the volatilisation of stannic sulphide during the roasting, see C. J. Brooks, *Chem. News*, **73**, 218, 1896.

[4] That is, sulphates derived from the oxidation of the sulphide. F. Henz, *Zeit. anorg. Chem.*, **37**, 39, 1903.

[5] H. Rose, *Ausführliches Handbuch der analytischen Chemie*, Braunschweig, **2**, 284, 1851; *Pogg. Ann.*, **112**, 163, 1861.

[6] It is generally used when but minute traces have to be determined gravimetrically.

[7] C. Mène, *Compt. rend.*, **31**, 82, 1850; *Dingler's Journ.*, **117**, 230, 1850; K. Pellet and A. Allart, *Bull. Soc. chim.*, (2), **27**, 43, 438, 1877; J. A. Sanchez, *ib.*, (4), **7**, 890, 1910; H. Nelsmann, *Zeit. anal. Chem.*, **16**, 50, 1877; L. Smith, *ib.*, **61**, 113, 1922; R. L. Hallett, *Journ. Soc. Chem. Ind.*, **35**, 1087, 1916; H. J. B. Rawlins, *Chem. News*, **107**, 53, 1913.

[8] STANDARD FERRIC CHLORIDE.—Dissolve, say, 37 grms. of piano wire in hydrochloric acid; oxidise with nitric acid or hydrogen peroxide; evaporate twice to dryness and dissolve in 200 c.c. of hydrochloric acid. Make the solution up to a litre. Or evaporate 90 grms. of pure commercial ferric chloride to dryness with hydrochloric acid; dissolve the residue in 150 c.c. of hydrochloric acid and make the solution up to a litre. Standardise by dissolving a gram of pure tin in hydrochloric acid as indicated for tin in the text.

[9] This is the converse of J. Löwenthal and A. Stromeyer's process for iron (R. Fresenius, *Anleitung zur quantitativen chemischen Analyse*, Braunschweig, **1**, 365, 1875).

The solution is filtered and neutralised with thin strips of zinc, whereby the tin and lead are precipitated. When the action is over and a drop of the clear filtrate gives no reaction for tin with "hydrogen sulphide water," pour off the clear liquid and wash the residue twice by decantation so as to keep the precipitated metals in the flask.[1]

The Titration.—Add 180 c.c. of hydrochloric acid (sp. gr. 1·16), and protect the contents of the flask from oxidation by a Bunsen valve (page 170). Heat the solution to boiling[2] and, when everything is dissolved, titrate while boiling with the standard solution of ferric chloride. The titration should be conducted rapidly, since the stannous chloride is very sensitive to oxidising agents, *e.g.* oxygen dissolved in the water.[3] Indeed, it is advisable to conduct the dissolution of the tin, and the titration, wholly in an atmosphere of carbon dioxide. The end of the reaction is indicated when a drop of ferric chloride imparts a permanent pale yellow tinge to the solution.

The End-Point.—F. Mohr, one of the pioneers in volumetric analysis,[4] says that, "in Mène's process, the coloration of the solution by the ferric chloride is not sufficiently marked to enable the operator to recognise with certainty if a drop be added in excess." With moderately concentrated solutions, a person with normal colour vision will soon recognise the effect when one drop of the ferric chloride has been added in excess, but with dilute solutions of ferric chloride Mohr's objection is quite valid. However, Morgan[5] has shown that if a blue Bunsen flame be examined by looking through the solution under titration, it will appear to have a greenish colour as soon as a trace of ferric chloride is in the solution. Morgan claims that a solution containing the equivalent of 0·00005 grm. of ferric oxide in 25 c.c. of water can be so recognised. The blue flame of a small Bunsen burner is placed about 13 mm. below the bottom of the flask in which the solution is being titrated. A good clear glass flask must be used, and the titration conducted in a darkened room, or in a dark corner.

Errors.—Mohr also points out that "Mène has stated, but not proved, that the decomposition is complete. A reverse action between the stannic chloride and the ferrous chloride proceeds very slowly in the cold, and is more marked on boiling. The reaction is only complete if an appreciable excess of ferric chloride be present. On the other hand, ferric chloride is wholly reduced by an equivalent quantity of stannous chloride; but stannous chloride cannot be oxidised by an equivalent, but only by an excess of ferric chloride." As a matter of fact, the results are very good when precautions are taken to prevent oxidation of the stannous chloride either during or before the titration. Molybdenum, antimony, titanium and tungsten interfere with the ferric chloride titration; uranium does not interfere. The titration in the presence of uranium wants careful watching, since the uranous salts are peroxidised *after* the tin and form a yellow solution. The ferric chloride tint gradually fades

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[1] If no zinc is present, add a small piece to fill the flask with an atmosphere of hydrogen.

[2] Do not boil too vigorously, or the hydrochloric acid will be weakened in strength before all the tin is dissolved.

[3] A. C. Campbell, *Journ. Anal. App. Chem.*, 2, 287, 1888.

[4] F. Mohr, *Lehrbuch der chemisch-analytischen Titriermethode*, Braunschweig, 264, 1874.

[5] F. H. Morgan, *Journ. Anal. App. Chem.*, 2, 169, 1888; C. L. H. Schwarz (*Praktische Anleitung zur Massanalysen*, Braunschweig, 132, 1853) added a drop of potassium thiocyanate to the solution and titrated until a persistent red tint appeared; C. Victor (*Chem. Ztg.*, 29, 179, 1905) titrates until starch and potassium iodide indicator is blued. W. Schuttlig (*Zeit. anal. Chem.*, 70, 55, 1927) uses indigo-carmine as an internal indicator and titrates in a solution containing at least 50 per cent. of concentrated hydrochloric acid until the indigo-blue colour appears.

as the uranium is peroxidised. Rawlins obtained a maximum error of 0·15 per cent. by the process.

Löwenthal and Stromeyer's Process.—Owing to the difficulty in determining the end-point when more dilute ferric chloride solutions are used, many prefer the Löwenthal modification,[1] where an excess of the standard ferric chloride is added to the solution. The stannous chloride reduces part of the ferric to ferrous chloride. The amount of ferrous chloride so formed is determined by the permanganate titration—Reinhardt's process, page 498. The chemical equation $2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$ corresponds with the fact that 1 grm. of potassium permanganate represents 2·3840 grms. of stannic oxide—SnO_2— in the given solution.

§ 148. Lenssen's Volumetric Iodine Process for Tin.

In Lenssen's iodine process,[2] the stannous chloride is titrated in an alkaline [3] solution with a standard solution of iodine. The results are apt to be very slightly low. This is due to the action of air on the stannous chloride, and it is generally considered best to work by the Pearce-Low method with acid solutions, which do not oxidise so readily as alkaline solutions. By carrying out the reduction and titration in an atmosphere of carbon dioxide, the risk of reoxidation is negligible. The reaction is generally represented by the equation:

$$SnCl_2 + I_2 + 2HCl = SnCl_4 + 2HI$$

This is supposed by Young to take place in two stages: (1) $2SnCl_2 + 2I_2 = SnCl_4 + SnI_4$, when an excess of stannous chloride is present; and (2) the reduction of stannic iodide to stannous iodide by the stannous chloride— $SnI_4 + 2SnCl_2 = 2SnI_2 + SnCl_4$.

Reduction of the Stannic to Stannous Chloride.—Hallett recommends the following procedure. The solution should contain not less than 25 nor more than 40 per cent. by volume of free hydrochloric acid. Accordingly, the

[1] J. Löwenthal, *Journ. prakt. Chem.*, (1), 76, 484, 1859; A. Stromeyer, *Liebig's Ann.*, 117, 261, 1861; C. Zengelis (*Ber.*, 34, 2046, 1901) titrates the excess of ferric chloride with stannous chloride until a drop of the solution colours a drop of ammonium molybdate blue; and T. Moore (*Chem. News*, 67, 267, 1893) titrates the excess of ferric chloride with cuprous chloride. For methylene blue indicator, see C. Russo, *Gazz. Chim. Ital.*, 44, i, 1, 1914; F. W. Atack, *Journ. Soc. Dyers and Colorists*, 29, 1, 1913. J. G. F. Druce (*Chem. News*, 128, 273, 1924) titrates the resulting ferrous chloride with potassium dichromate, with diphenylamine as internal indicator (see page 502).

[2] G. de Claubry, *Compt. rend.*, 23, 101, 1846: J. A. Müller, *Bull. Soc. chim.*, (3), 25, 1002, 1901; *Chem. News*, 85, 114, 1902; A. Fraenkel and J. Fasal, *Mitt. K. K. Tech. Gew. Wien*, 7, 227, 1897; A. Scheurer-Kestner, *Chem. News*, 4, 101, 192, 1861; F. Ibbotson and H. Brearley, *ib.*, 84, 167, 1901; E. Lenssen, *Journ. prakt. Chem.*, (1), 78, 200, 1859; *Liebig's Ann.*, 114, 114, 1860; G. Topf, *Zeit. anal. Chem.*, 26, 163, 1887; C. Friedheim, *Zeit. anorg. Chem.*, 4, 145, 1893; W. H. Low, *Journ. Amer. Chem. Soc.*, 29, 66, 1907; S. W. Young and M. Adams, *ib.*, 19, 515, 1897; S. W. Young, *ib.*, 19, 845, 851, 1897; 23, 21, 119, 453, 1901; R. Job, *Journ. Soc. Chem. Ind.*, 17, 325, 1898; T. Benas, *Zur massanalytischen Bestimmung des Zinns und über einige Zinnoxydulsalze*, Berlin, 1884; J. A. Sanchez, *Bull. Soc. chim.*, (4), 7, 890, 1910; H. J. B. Rawlins, *Chem. News*, 107, 53, 1913; A. Fraenkel and J. Fasal, *ib.*, 78, 100, 1898; A. Jolles, *Chem. Ztg.*, 12, 597, 1888; W. B. Patrick and G. C. Wilsnack, *Journ. Ind. Eng. Chem.*, 4, 597, 1912; R. L. Hallett, *Journ. Soc. Chem. Ind.*, 35, 1087, 1916; N. Welwart, *Chem. Ztg.*, 40, 458, 1916; J. G. F. Druce, *Chem. News*, 121, 173, 1920; B. Köhler, *Chem. Listy*, 16, 87, 1922; B. S. Evans, *Analyst*, 52, 590, 1927; R. Höltje, *Zeit. anorg. Chem.*, 198, 287, 1931; D. Lombardo, *Met. Ital.*, 24, 10, 1932; D. B. Dott, *Pharm. Journ.*, (4), 27, 486, 1908; P. E. Winkler, *Bull. Soc. chim. Belg.*, 41, 115, 1932; F. W. Louw and W. E. Schilz, *Journ. S. African Chem. Inst.*, 17, 3, 1934.

[3] In the presence of potassium sodium tartrate and sodium bicarbonate.

hydrochloric acid solution of the stannic chloride is evaporated to about 50 c.c. in a 350 c.c. wide-mouthed conical beaker, or, alternatively, 0·5 to 2 grms. of the sample are dissolved in hydrochloric acid. 50 c.c. of concentrated hydrochloric acid (sp. gr. 1·16) and 200 c.c. of water are added. A coil of nickel foil,[1] 10 cm. by 4 cm., in a loose roll, with a strip to serve as a handle, is inserted into the beaker. The projecting end of the strip is folded over the rim of the beaker, which is then covered with a clock-glass. Boil the solution for 30 minutes, after any iron present has been reduced. Add two small cubes of marble to the solution to produce an atmosphere of carbon dioxide and cool below 22°. Remove the nickel foil from the solution and rinse it with hydrochloric acid (1 in 3).

The Titration.—Add a few drops of starch paste (page 285) to the solution, and titrate the mixture *rapidly* with a standard solution of iodine[2] until the blue colour of the starch appears. For details of the "iodine" titration, see page 367. Nickel, cobalt, manganese, molybdenum, uranium, chromium, aluminium, zinc, lead, calcium, magnesium, sulphates, phosphates, bromides, iodides and fluorides do not interfere unless their colour is sufficient to mask that of the indicator. Trivalent arsenic and antimony consume iodine in dilute acid solution, but have no effect in an acid solution of the strength used. Antimony in excess of 0·1 grm. will be precipitated during the reduction in a slimy form which does not settle and obscures the end-point. Precipitation can be prevented by increasing the amount of hydrochloric acid to 75 c.c. Copper in quantities greater than 0·05 grm. will be incompletely precipitated and iodine will be consumed by that which remains in solution; hence copper must be removed. Bismuth, tungsten and titanium, in any reasonable amount such as is usually met with, do not interfere with the method, especially if the titration is performed rapidly. The interference of all these metals is greatly increased by very slow and careful titration, which seems to accelerate their reaction and gives time for the result to be affected seriously. This applies particularly to titanium. Ferrous chloride is oxidised only by an excess of iodine. Ibbotson and Brearley's test analyses with the powdered "antimony reduction" show:—

Tin used	.	0·1750	0·1000	0·0480	0·0200	0·0080 grm.
Tin found	.	0·1752	0·0997	0·0490	0·0201	0·0083 grm.

Rawlins obtained a maximum error of 0·10 per cent. by the process. In all volumetric processes for tin, there is a tendency to low results owing to the rapidity with which the reduced tin salt is oxidised.[3]

[1] C. and J. J. Beringer, *A Textbook of Assaying*, London, 288, 1906; R. L. Hallett, *Journ. Soc. Chem. Ind.*, 35, 1087, 1916. For reduction by aluminium, see R. Höltje, *Zeit. anorg. Chem.*, 198, 287, 1931; J. A. Sanchez, *Bull. Soc. chim.*, (4), 7, 890, 1910: by antimony, see F. Ibbotson and H. Brearley, *Chem. News*, 84, 167, 1901: by iron, see W. B. Patrick and G. C. Wilsnack, *Journ. Ind. Eng. Chem.*, 4, 597, 1912; H. Wolf and R. Heilingötter, *Chem. Ztg.*, 53, 683, 1929; D. Lombardo, *Met. Ital.*, 24, 10, 1932; R. Höltje, *loc. cit.* Note that the carbon present in iron generally causes high results, hence pure, soft iron must be used. By lead, see A. R. Powell, *Journ. Soc. Chem. Ind.*, 37, 285, 1918; B. S. Evans, *Analyst*, 52, 590, 1927; S. G. Clarke, *ib.*, 56, 82, 1931. B. S. Evans (*Analyst*, 56, 171, 1931) advocates the use of hypophosphorous acid.

[2] Page 287. About 21·39 grms. of iodine and 45 grms. of potassium iodide are made up to a litre. One c.c. of this solution will represent about 0·01 grm. of tin. The solution should, however, be standardised against a known weight of pure tin.

[3] E. A. Lewis, *London Min. Journ.*, 606, 1911.

§ 149. Classen and Henz's Electrolytic Process for Tin.

Tin is readily deposited from solutions of ammonium oxalate in the presence of an excess of oxalic acid.[1] If ammonium oxalate be used alone, it is converted during the electrolysis into ammonium carbonate. The electrolyte then smells of ammonia, and stannic acid may separate, particularly if much tin be present. The stannic acid is dissolved by an excess of oxalic acid. Hence the electrolyte must always be kept acid by the addition of, say, oxalic acid.

The Electrolyte.—In gravimetric analysis the tin is obtained as sulphide, and it is usually dissolved in sodium sulphide. To convert this solution into acid oxalate, acidify the solution with dilute acetic acid; dissolve equal parts of ammonium oxalate and oxalic acid in hot water, so that the total amount of oxalate and oxalic acid per 0·1 grm. of tin amounts to 3·5 grms; heat the solutions to boiling and pour the oxalate-oxalic acid solution into the tin solution. The resulting solution may be slightly turbid owing to the separation of some sulphur, but it forms an excellent electrolyte for the deposition of tin.

The Electrolysis.—Use a current density of about 0·2 to 0·3 amp., and an E.M.F. of 2 to 3 volts. In about six hours most of the tin will have deposited. Add 8 c.c. of sulphuric acid (1 : 1) (or add more oxalic acid), and continue the electrolysis for another twenty-four hours. All the tin will then probably be precipitated.[2] Engels says that the electrolysis can be shortened by the addition of hydroxylamine sulphate to the electrolyte (see page 259).

Results.—The tin is precipitated as a compact shining silver-white metal. It is washed, dried and weighed as usual. In illustration of the results, Henz gives the subjoined numbers (*Table XLIV.*)

The table shows that the proportions indicated above are likely to give satisfactory results.[3] The time factor is a rather serious objection.

Removal of Tin from the Electrode.—There is a difficulty in removing tin from the cathode, since the metal does not readily dissolve in acids—even boiling hydrochloric acid dissolves the metal very slowly. Nitric acid forms a coating of stannic oxide, which must be frequently removed in order to expose a fresh surface of the metal to attack. Classen recommends warming the deposit with a mixture of 2 grms. of tartaric acid, 8 c.c. of water and 2 c.c. of concentrated nitric acid; or fusion with potassium bisulphate. Some recom-

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[1] F. Henz, *Zeit. anorg. Chem.*, **37**, 31, 1903; A. Fischer, *ib.*, **42**, 363, 1904; J. M. M. Dormaar, *ib.*, **53**, 349, 1907; A. Classen and O. Bauer, *Ber.*, **16**, 1061, 1883; A. Classen and M. A. von Reis, *ib.*, **14**, 1622, 1881; A. Classen, *ib.*, **17**, 2467, 1884; **18**, 1110, 1885; **27**, 2060, 1894; M. Heidenreich, *ib.*, **28**, 1586, 1895; C. Engels, *Elektrochem. Zeit.*, **2**, 418, 1896; A. Scheen, *ib.*, **14**, 257, 1908; F. Förster and J. Wolf, *ib.*, **13**, 205, 1907; H. J. S. Sand, *ib.*, **13**, 327, 1907; H. Ost, *Zeit. angew. Chem.*, **10**, 325, 1897; **14**, 817, 1901; A. Hollard, *Bull. Soc. chim.*, (3), **29**, 262, 1903; A. Inhelder, *Beitrag zur Trennung des Antimons und Zinns und zur Analyse von Lagermetallen*, Zürich, 1911; A. H. Cushman and E. B. Wettengel, *Journ. Ind. Eng. Chem.*, **5**, 217, 1913; F. Rüdorff, *Zeit. angew. Chem.*, **5**, 3, 197, 1892; E. D. Campbell and E. C. Campion, *Journ. Amer. Chem. Soc.*, **20**, 687, 1898; H. E. Medway, *Amer. Journ. Sci.*, (4), **18**, 57, 1904; B. Pasztor, *Elektrochem. Zeit.*, **16**, 281, 1910; E. P. Schoch and D. J. Brown, *Eighth Inter. Cong. App. Chem.*, **21**, 81, 1912; L. Bertiaux, *Ann. Chim. anal.*, **18**, 217, 1913; E. Eckert, *Metall u. Erz*, **21**, 202, 1924; J. Svéda and R. Uzel, *Coll. Czech. Chem. Comm.*, **4**, 203, 1929; T. Batuecas, *Anal. Fis. Quim.*, **14**, 495, 1916.

[2] To make sure, withdraw about 1 c.c. by means of a pipette; acidify the solution with sulphuric acid, add "H_2S water," and warm gently. If brown or yellow stannous or stannic sulphides separate, the electrolysis is not completed. Do not confuse free sulphur with tin sulphide.

[3] It is, however, significant to note that a Beit fellowship for scientific research was awarded in 1932 "for research on the electro-deposition of tin with the view of establishing the precise conditions under which crystalline deposits may be obtained and avoiding the unsatisfactory spongy deposits which result from present processes."—*Nature*, **130**, 89, 1932.

Table XLIV.—Test Analyses with the Electrolytic Process for Tin.

Used Sn. Gram.	Current density. Amp.	Ammonium oxalate. Grams.	Sulphuric acid added.		Total duration of the electrolysis. Hours.	Found Sn. Gram.	Error.	
			After hours.	c.c.			Gram.	Per cent.
0·1017	0·75–1·00	15	5½	10	28	0·1036	+ 0·0019	1·9
0·1017	0·48–0·05	15	3	10	27	0·1021	+ 0·0004	0·4
0·2555	0·35–0·24	15	7	10	24	0·2555	0·0000	0·0
0·2555	0·38–0·20	15	8	10	24	0·2548	– 0·0007	0·3
0·2555	0·30–0·10	15	7½	10	23	0·2550	– 0·0005	0·2
0·2555	0·38–0·20	30	3	5	22	0·2551	– 0·0004	0·2
0·1017	0·15–0·10	15	6	2	21	0·1016	– 0·0001	0·1

mend coating the cathode with a film of copper, silver or cadmium before precipitating the tin in order to prevent the platinum being seriously attacked during the subsequent removal of the deposited tin. Another plan is to make the dish the anode and electrolyse a solution of dilute sulphuric acid with a piece of copper wire as cathode.

§ 150. Miscellaneous Processes for Tin.

Other processes for the determination of tin depend upon the titration of a reduced solution with potassium bromate, potassium iodate, potassium permanganate or chloramine.[1] Cupferron has also been proposed as a precipitant for stannous or stannic tin.[2]

§ 151. The Evaluation of Commercial Compounds containing Tin.

Tin Oxide.—The amount of tin oxide can be determined by reducing the sample to metal in a current of hydrogen or coal gas [3] (page 266), and dissolving the metal in hydrochloric acid. The solution may be titrated for tin as indicated above. The metal may also be obtained by reduction with potassium cyanide (page 268). The button of metal should be specially analysed for tin, since it may be contaminated with other metals.[4]

The following method is rapid and has been found to give good results:—

Opening-up the Sample.—Weigh out exactly 0·25 grm. of the dry (110°) sample in a nickel crucible and mix it with about 3 grms. of sodium peroxide. Heat the crucible with a small flame, after covering it with a lid. Continue to heat and gradually increase the flame until the contents are in a state of quiet fusion. Cool. When cold, place the crucible and lid in a beaker. Cover the beaker with a clock-glass and introduce water through the lip of the beaker

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[1] Bromate process, see F. Fichter and E. Muller, *Chem. Ztg.*, **37**, 309, 1913; V. Velich, *Chem. Listy*, **15**, 5, 38, 56, 1921. Iodate, see G. S. Jamieson, *Journ. Ind. Eng. Chem.*, **8**, 500, 1916. Permanganate, see K. Someya, *Zeit. anorg. Chem.*, **160**, 404, 1927. Chloramine, see E. Rupp, *Zeit. anal. Chem.*, **73**, 51, 1928; E. Rupp and F. Lewy, *ib.*, **77**, 1, 1929.

[2] A. Pinkus and J. Claessens, *Bull. Soc. chim. Belg.*, **36**, 413, 1927; N. I. Chervyakov and E. A. Ostroumov, *Ann. Chim. anal. Chim. appl.*, **18**, 201, 1936.

[3] For reduction by alcoholic vapours, see G. L. Chaborski and M. M. Badescu, *Bul. Chim. Soc. Române Chim.*, **32**, 7, 1929.

[4] See also footnote 3, page 268.

from a pipette. When the cake has been decomposed, boil gently for a few minutes. Remove the clock-glass and wash its under side into the beaker. Then remove the crucible and lid and rinse each well with hot distilled water. Cover the beaker with a clock-glass and gradually add concentrated hydrochloric acid to the contents of the beaker with stirring, until a clear green solution is obtained; then rinse the under side of the clock-glass into the beaker.

Reduction to Stannous Chloride.[1]—Transfer the solution to a conical flask and dilute, if necessary, to about 200 c.c. Add 100 c.c. of concentrated hydrochloric acid [2] and about 2 grms. of antimony powder, which has been ground in an agate mortar until it is free from all glistening particles. Now heat the liquid and boil vigorously for five minutes, so that the antimony powder is projected well up into the liquid.

The Titration.—Cool the flask and contents as rapidly as possible in a current of cold water and at the same time pass a rapid stream of carbon dioxide through the solution to prevent reoxidation. When cold, add a small chip of marble and 10 c.c. of starch solution. Titrate at once with 0·1N-iodine solution until a blue colour is obtained which lasts for about two minutes. Since 1 c.c. of 0·1N-iodine represents 0·007535 grm. of stannic oxide, SnO_2, if v c.c. of iodine solution be used, the percentage of tin dioxide in the sample is 3·014 v.[3]

Tin Ash (Calcine).—Here, tin and lead are to be separated. The hydrochloric acid solution is treated with an excess of sodium hydroxide, and saturated with hydrogen sulphide. Lead is precipitated; tin remains in solution. The tin solution may be treated as indicated on pages 313–315; the lead sulphide as on page 329.[4]

Sodium Stannate.—Commercial sodium stannate may contain relatively large quantities of sodium arsenate.[5] The analyst may thus have to determine both the tin and the arsenic. The arsenic may be precipitated by placing best piano wire in the solution acidified with hydrochloric acid, as in the case of antimony by Tookey's process. The tin can be determined in the filtrate. The sodium can be determined as chloride by applying part of the process given on page 217.

[1] F. Ibbotson and L. Aitchison, *The Analysis of Non-ferrous Alloys*, London, 106, 1922.

[2] Trivalent antimony and arsenic are not oxidised by iodine in strongly acid solution—F. Ibbotson and L. Aitchison (*l.c.*).

[3] See also footnote 2, page 319.

[4] For the solubility of lead sulphate in stannous chloride, see M. de Jong, *Zeit. anal. Chem.*, **41**, 596, 1902; A. van Raalte, *ib.*, **43**, 36, 1904.

[5] E. Haeffely (*Phil. Mag.*, (4), **10**, 220, 1855) adds a known excess of arsenic, boils with an excess of nitric acid, weighs the tin as tin arsenate—$2SnO_2.As_2O_5$—and determines the excess of arsenic in the filtrate. See T. Goldschmidt, *Dingler's Journ.*, **162**, 77, 1861; A. Scheurer-Kestner, *Répertm. Chim. App.*, **4**, 221, 1862; P. T. Austen, *Amer. Chem. Journ.*, **5**, 210, 1883.

CHAPTER XXIV.

THE DETERMINATION OF LEAD.

§ 152. The Properties of Lead Sulphate.

LEAD is perhaps most frequently separated and weighed as sulphate. Lead sulphate is a heavy white powder sparingly soluble in water: 100 c.c. of water dissolve nearly 0·0038 grm. lead sulphate at 15°.[1] The solubility is decreased in the presence of small quantities of sulphuric acid and increased in more concentrated solutions, as well as in solutions of hydrochloric and nitric acids. This is illustrated by the following table[2]:—

Table XLV.—Solubility of Lead Sulphate in Mineral Acids.

Sulphuric acid.		Nitric acid.		Hydrochloric acid.	
Grm. PbSO₄ per 100 grms. sol.	Normality of acid.	Grm. PbSO₄ per 100 grms. sol.	Normality of acid.	Grm. PbSO₄ per 100 grms. sol.	Normality of acid.
0·003	20·0	0·33	2·40	0·14	2·93
0·011	31·5	0·59	3·60	0·35	4·77
0·039	36·4	0·78	7·90	0·95	6·66

The effect of sulphuric acid in reducing the solubility of lead sulphate is illustrated by the graph, fig. 89. It is generally supposed that lead sulphate is best precipitated from a liquid approximately normal with respect to sulphuric acid, and the precipitate is best washed with an acid of the same strength. Huybrechts and Ramelot (*l.c.*) say that the solubility of lead sulphate in solutions of sulphuric acid, sodium sulphate or ammonium sulphate is a minimum (3 to 4 mgrms. per litre at 18°) at concentrations of 0·01 to 0·05 M.

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[1] H. C. Dibbits, *Zeit. anal. Chem.*, 13, 139, 1874; F. Kohlrausch, *Zeit. phys. Chem.*, 50, 356, 1905; W. Böttger, *ib.*, 46, 602, 1903; R. Fresenius, *Liebig's Ann.*, 59, 125, 1876; G. F. Rodwell, *Chem. News*, 11, 50, 1865; M. Pleissner, *Ueber die Loslichkeit einiger Bleiverbindungen in Wasser*, Berlin, 1903.

[2] Schultz, *Pogg. Ann.*, 113, 137, 1861; G. F. Rodwell, *Journ. Chem. Soc.*, 15, 59, 1862; C. S. Sellack, *Pogg. Ann.*, 133, 137, 1868; *Zeit. anal. Chem.*, 9, 464, 1870: H. Struve, *ib.*, 9, 34, 1870; W. Städel, *ib.*, 2, 180, 1863; C. Stammer, *Dingler's Journ.*, 165, 209, 1862; *Chem. Ztg.*, 6, 63, 1884; J. Sehnal, *Compt. rend.*, 148, 1394, 1909; K. Beck and P. Stegmüller, *Arb. Kais. Gesund. Amt.*, 34, 446, 1910; M. Pleissner, *ib.*, 26, 384, 1907; L. L. de Koninck, *Bull. Soc. chim. Belg.*, 21, 141, 1907; M. G. Donk, *U.S. Dept. Agr. Bull.*, 90, 1905; H. Ditz and F. Kanhäuser, *Zeit. anorg. Chem.*, 98, 128, 1916; M. Huybrechts and H. Ramelot, *Bull. Soc. chim. Belg.*, 36, 239, 1927; A. E. Dawkins and P. R. Weldon *Proc. Soc. Chem. Ind. Victoria*, 22, 940, 1922.

Accordingly, they recommend that the solution, prior to filtration, should contain about 0·3 per cent. of free sulphuric acid and that the precipitate should be washed with a solution of this concentration. The solubility of lead sulphate is also reduced in the presence of alcohol. Hence many prefer to dilute the liquid with two or three times its volume of alcohol or methylated spirit, and wash with a dilute alcoholic solution of sulphuric acid containing 10 per cent. of alcohol and 1 per cent. of sulphuric acid, in order to reduce the loss of lead sulphate to a minimum. There is little difference in the actual results with the alcohol and the dilute sulphuric acid treatments, but the use of alcohol is apt to give high results, because very few sulphates are readily soluble in alcohol. According to Sehnal, lead sulphate is "absolutely insoluble
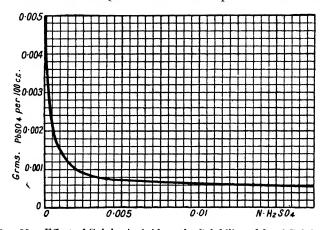
Fig. 89.—Effect of Sulphuric Acid on the Solubility of Lead Sulphate.

in water containing one part of H_2SO_4 per 1000 c.c." If "absolutely" here means that "the amount of soluble lead sulphate cannot be determined by ordinary analytical methods," the statement is correct.

The solubility of lead sulphate is increased in the presence of alkali chlorides and many other salts. It is fairly soluble in ammonium acetate,[1] tartrate, citrate, chloride and nitrate, and in sodium thiosulphate, sodium acetate and caustic alkalies.[2] In illustration, the following table represents the solubility of lead sulphate in ammonium acetate (Noyes and Whitcomb) and in sodium acetate (Dunnington and Long). The solubility is increased by raising the temperature.

It is therefore necessary to precipitate lead sulphate from solutions as free as possible from, inter alia, ammonium salts, alkali chlorides, nitric and hydrochloric acids. If potassium salts be present, Levol [3] has pointed out that there is a danger of precipitating potassium sulphate with the lead sulphate in

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[1] L. Kahlenberg, Zeit. phys. Chem., 17, 577, 1895; J. Löwe, Journ. prakt. Chem., (1), 74, 348, 1858; A. A. Noyes and W. H. Whitcomb, Journ. Amer. Chem. Soc., 27, 747, 1905; C. Blomberg, Chem. Weekblad, 11, 1030, 1914; J. W. Marden, Journ. Amer. Chem. Soc., 38, 310, 1916; Anon, Chem. News, 1, 132, 1860.

[2] H. C. Dibbits, Bull. Soc. chim., (2), 20, 258, 1873; F. P. Dunnington and J. C. Long, Amer. Chem. Journ., 22, 217, 1899; E. Lenssen, Journ. prakt. Chem., (1), 85, 89, 1862; J. Löwenthal, ib., (1), 60, 267, 1853; J. J. Fox, Journ. Chem. Soc., 95, 878, 1909.

[3] A. Levol, Rép. Chim. App., 4, 21, 1862; Chem. News, 5, 144, 1862; J. J. Fox, Proc. Chem. Soc., 23, 199, 1907; Journ. Chem. Soc., 95, 878, 1909; F. G. Belton, Chem. News, 91, 191, 1905; Z. Karaglanov, Zeit. anal. Chem., 106, 262, 1936.

Table XLVI.—Solubility of Lead Sulphate in Ammonium and Sodium Acetates.

Ammonium acetate.				Sodium acetate.	
25°		100°		100°	
Grm. PbSO₄ per 100 c.c.	Grm. acetate per 100 c.c.	Grm. PbSO₄ per 100 c.c.	Grm. acetate per 100 c.c.	Grm. PbSO₄ per 100 c.c.	Grm. acetate per 100 c.c.
0·0041	0·000	7·12	28	0·054	2·05
0·0636	0·798	9·88	32	0·853	8·20
0·138	1·596	10·58	37	11·23	41
0·302	3·192	11·10	45	..	..

the form of a double lead and potassium sulphate— $K_2Pb(SO_4)_2$. There is not the same risk with sodium sulphate.

The solubility of lead sulphate in sodium thiosulphate and ammonium acetate solutions is frequently used in separating lead sulphate from barium sulphate. The latter is supposed to be insoluble in ammonium acetate and sodium thiosulphate. When sodium thiosulphate is used, the temperature must be kept below 20°, or an insoluble lead sulphide may be formed.[1] If basic iron sulphate [2] or barium sulphate [3] be precipitated with the lead sulphate, there is a difficulty in dissolving the last traces of the lead sulphate in ammonium acetate, thus leading to low results. With ammonium acetate, there is a small error owing to the slight solubility of barium sulphate in this menstruum. Kernot [4] finds that at 25° the solubility of barium sulphate reaches its maximum (0·133 grm. per litre) in a 30 per cent. solution of ammonium acetate and then falls as the concentration of the solution increases. Solutions of carbonates and of bicarbonates [5] convert lead sulphate at ordinary temperatures into lead carbonate, which is soluble in dilute nitric or acetic acid. This reaction is also sometimes used for separating lead sulphate from barium sulphate (see page 579), which does not react with carbonates in the same way.[6]

Lead sulphate is practically unaltered when exposed to the air, and also when ignited at a low red heat. It fuses at about 1100° without decomposition, provided reducing agents be absent.[7] If heated for a long time there may be

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[1] J. Löwe, *Journ. prakt. Chem.*, (1), **77**, 75, 1859.

[2] J. H. Walton and H. A. Scholz, *Amer. Chem. Journ.*, **39**, 771, 1908; *Chem. News*, **98**, 61, 76, 1908.

[3] J. C. Bull, *School Mines Quart.*, **23**, 348, 1903; *Chem. News*, **87**, 40, 52, 66, 1903.

[4] G. Kernot, *Rend. Accad. Sci. Napoli*, (3), **15**, 155, 1909. E. Erlenmeyer (*Biochem. Zeit.*, **56**, 330, 1913) separates lead sulphate from calcium sulphate by treating with equal volumes of a saturated solution of ammonium acetate and 96 per cent. alcohol, in which lead sulphate is eight times more soluble than the calcium salt.

[5] H. Rose (*Pogg. Ann.*, **95**, 426, 1855) says that bicarbonates do not dissolve lead.

[6] In a glass containing silica, lead and barium, etc. these three can be obtained as precipitates on the filter-paper after evaporation with sulphuric acid. The lead sulphate is then converted into lead carbonate, which is removed by acetic acid; the residue of silica and barium sulphate is ignited and weighed. The silica is then expelled by evaporation with hydrofluoric acid and, after ignition, the barium sulphate weighed. The lead is determined by titration or gravimetrically.

[7] O. L. Erdmann, *Journ. prakt. Chem.*, (1), **62**, 381, 1854.

an appreciable loss by volatilisation.[1] Thus, 1·4082 grms., when heated in a porcelain tube in a current of carbon dioxide, lost in weight, according to Williams, 0·134 per cent. either by volatilisation or partial decomposition.

§ 153. The Determination of Lead as Sulphate.

The solution is evaporated with about 10 c.c. of concentrated sulphuric acid [2] until the total volume is reduced to approximately 3 c.c. If present, nitric or hydrochloric acid, which increase the solubility of the lead sulphate, will incidentally be expelled during the evaporation. Cool the solution. Add water until the volume of the liquid is about 100 c.c., thus giving a solution of about 1·0N-strength. Stir and stand, then filter through a Gooch crucible packed with asbestos or, better, through a Munroe crucible,[3] since there is a risk of the acid attacking asbestos. Wash the precipitate with dilute sulphuric acid (0·5N- to N-H_2SO_4) [4] and finally with alcohol, until the washings are free from sulphuric acid.[5] Dry the precipitate over a burner with a mushroom head and finally ignite for a short time over a Bunsen burner [6] at a dull red heat. When cold, weigh the ignited precipitate as lead sulphate—$PbSO_4$—and add to the weight 0·0006 grm., this being the solubility of the salt in 100 c.c. of 1·0N-H_2SO_4. The weight of the lead sulphate multiplied by 0·7360 represents the corresponding amount of lead oxide—PbO—or use fig. 14. The results are usually excellent.[7]

§ 154. The Separation of Lead from Bismuth, Copper and Cadmium.

The process just indicated gives excellent separations of lead from copper, cadmium and zinc. We therefore take up the problem left on page 277: the separation of the constituents of the residue left on treatment of the hydrogen sulphide precipitate with sodium monosulphide. The residue is dissolved in concentrated hydrochloric acid. The procedure now varies according as bismuth is present or absent, for bismuth is so like lead in its general behaviour

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[1] C. P. Williams, *Chem. News*, **23**, 236, 1871; A. Mitscherlich, *Journ. prakt. Chem.*, (1), **83**, 485, 1861; J. Boussingault, *Compt. rend.*, **64**, 1159, 1867.

[2] Be careful in adding concentrated acid to dilute solutions, or some liquid may be lost by spurting.

[3] Filter-paper can be used to collect the lead sulphate. In that case, dry the washed precipitate; separate the precipitate from the paper on a watch-glass; burn the paper in a weighed crucible; moisten the ash with nitric acid; add a drop of sulphuric acid; evaporate to dryness on a low flame. Transfer the precipitate from the watch-glass to the crucible and ignite over the Bunsen burner to a constant weight.

[4] L. L. de Koninck (*Bull. Soc. chim. Belg.*, **21**, 141, 1907) washes the precipitate with water containing 0·7 per cent. of ammonium sulphate.

[5] If the sulphuric acid be not washed out, particularly from filter-paper, the paper may be charred as the acid becomes more and more concentrated during the drying of the precipitate. With the Munroe crucible there is not so much need for the alcohol washing.
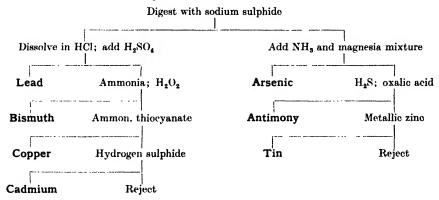
[6] Some merely dry the precipitate at 110° before weighing.

[7] According to A. G. Blakeley and E. M. Chance (*Journ. Soc. Chem. Ind.*, **30**, 518, 1911), in the ordinary method of precipitating lead as sulphate, the presence of tin and antimony interferes because basic salts are precipitated with the lead sulphate. P. H. Walker and H. A. Whitman, *Journ. Ind. Eng. Chem.*, **1**, 519, 1909; R. E. Lee, J. P. Trickey and W. H. Fegely, *Journ. Ind. Eng. Chem.*, **6**, 556, 1914. For the determination of lead as sulphate, see also L. W. Winkler, *Zeit. angew. Chem.*, **35**, 662, 715, 1922; Z. Karaglanov and B. Sagortschev, *Zeit. anal. Chem.*, **81**, 275, 1930. F. D. Miles (*Journ. Chem. Soc.*, **107**, 988, 1915) decomposes the precipitated lead sulphate with hydrogen sulphide and then titrates the liberated sulphuric acid.

that it is not easy to obtain clean separations and, if bismuth is present,[1] a more circuitous path must be taken.

(1) *Bismuth absent.*—This is nearly always the case in the analysis of pottery colours and glazes. The solution is evaporated on a water bath along with a little sulphuric acid. The evaporation is completed on a hot plate or over a ring burner, until the sulphuric acid begins to fume. The object is to drive off the hydrochloric acid, which leads to an imperfect precipitation of the lead sulphate. The lead sulphate is determined by diluting the solution as indicated for lead sulphate (page 326).

(2) *Bismuth present.*—The solution should contain just enough hydrochloric acid to prevent the precipitation of basic bismuth salts when the solution is diluted. The right amount of hydrochloric acid is determined [2] as follows:— Evaporate the solution on a water bath, and put a drop of the evaporating solution on a watch-glass with a drop of water. If no precipitate forms, too much hydrochloric acid *may* be present. Continue the evaporation. If a white precipitate forms, the evaporation has gone too far and hydrochloric acid is added, a few drops at a time, until no precipitate of basic bismuth salt forms when a drop of the solution is diluted with water. The lead is then precipitated as lead sulphate and the bismuth separated from the copper and the cadmium by Jannasch's process (page 362). If no bismuth be present, proceed to copper (page 365). The process just indicated for the separation of lead from bismuth, copper and cadmium requires great care and some practice before good results can be ensured. Some might prefer to employ Löwe's process for the separation of bismuth from copper, cadmium and lead, and afterwards separate the lead from the copper and cadmium in the form of lead sulphate. The separation of bismuth is discussed on page 360 *et seq.*[3]

The scheme for separating the constituents of the precipitate produced by hydrogen sulphide may now be conveniently summarised (mercury absent)— solids to left, solutions to right:—

Digest with sodium sulphide

Dissolve in HCl; add H₂SO₄	Add NH₃ and magnesia mixture

Lead	Ammonia; H_2O_2	**Arsenic**	H_2S; oxalic acid
Bismuth	Ammon. thiocyanate	**Antimony**	Metallic zinc
Copper	Hydrogen sulphide	**Tin**	Reject
Cadmium	Reject		

Any step can be omitted if the qualitative process shows the corresponding element is absent. The scheme for dealing with the next group is given on page 413.

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[1] For the detection of lead in bismuth, see G. Guérin, *Journ. Pharm. Chim.*, (7), **8**, 422, 1913.

[2] O. Steen, *Zeit. angew. Chem.*, **8**, 530, 1895; H. Rose, *Pogg. Ann.*, **110**, 432, 1860; C. Friedheim, *Leitfaden für quantitative chemische Analyse*, Berlin, 300, 1905; H. Herzog, *Journ. Anal. App. Chem.*, **1**, 245, 1887; *Chem. News*, **58**, 129, 1888.

[3] A. Patera (*Bull. Soc. chim.*, (2), **5**, 442, 1866) separated lead chloride from bismuth chloride by shaking out with a mixture of absolute alcohol and ether, in which the bismuth chloride alone dissolves.

§ 155. The Analysis of White Lead.

There are several alternative schemes for the analysis of white lead.[1] The following process brings out the information required from the chemical analysis for most technical operations:—

Hygroscopic Moisture.—Dry a weighing bottle in a steam oven; cool in a desiccator and weigh. Transfer about 10 grms. of the sample to the weighing bottle and weigh again. Dry the sample in the steam or air bath at from 100° to 105° until no further loss in weight occurs—overnight generally suffices—when further heated. The loss in weight represents hygroscopic moisture.[2]

Dissolution of the White Lead.—Transfer a gram of the dried sample to a 100 c.c. flask and boil for 5 minutes with an excess of dilute acetic acid.[3] Filter through a 6·5 cm. filter-paper and wash once with hot dilute acetic acid and then with hot water. The residue may contain insoluble sand (silica), silicates (clays), lead sulphate, barium sulphate, calcium sulphate and possibly alumina, magnesia and free lead.

The Soluble Portion.—Heat the solution; add 1 c.c. of a saturated solution of mercuric chloride.[4] Pass hydrogen sulphide through the boiling liquid for about half an hour.[5] Let the precipitate settle. Filter.[6] Wash with hot water.[7] The precipitate may contain zinc and lead sulphides; the filtrate, calcium, barium and possibly magnesium salts. Boil the filtrate to expel the hydrogen sulphide, and precipitate the barium with sulphuric acid (page 582) and filter. Calculate the corresponding amount of barium carbonate by multiplying the weight of barium sulphate by 0·8455. Precipitate the lime as oxalate (page 202), and calculate the corresponding amount of calcium carbonate by multiplying the weight of calcium oxide by 1·7846. Precipitate the magnesium as phosphate (page 205), and calculate the corresponding amount of magnesium carbonate by multiplying the weight of the magnesium pyrophosphate by the factor 0·7573.

[1] P. Drawe, *Zeit. angew. Chem.*, **15**, 174, 1902; A. Coppalle, *Ann. Chim. anal. app.*, **12**, 62, 1907; G. W. Thompson, *Journ. Soc. Chem. Ind.*, **24**, 487, 1905; G. Tissandier, *Chem. News*, **23**, 268, 1871; A. Neujean, *ib.*, **22**, 251, 1870; A. Adriani, *ib.*, **4**, 43, 1861; E. Euston, *Journ. Ind. Eng. Chem.*, 6, 382, 1914; K. Friedrich, *Metallurgie*, 9, 409, 1912; *Chem. Engineer*, **22**, 37, 1915; F. W. Glaze, *Chemist-Analyst*, **16**, 19, 1927; *Proc. Amer. Soc. Testing Materials*, **14**, (1), 269, 1914.

[2] W. A. Davis and C. A. Klein (*Journ. Soc. Chem. Ind.*, **26**, 848, 1907) say heat has no action below 110° and decomposition begins at 120°. L. Joulin (*Chem. News*, **27**, 211, 1873) considers that at temperatures over 50° there is no security against partial decomposition and loss of carbon dioxide. At 150° the pressure of cerussite was below 30 mm.; at 250°, 75 mm.; and at 300° decomposition was complete. We have met with only one sample of white lead which showed an appreciable decomposition when dried in the steam oven; usually drying in the steam oven is quite safe. A. Colson, *Compt. rend.*, **140**, 865, 1905.

[3] DILUTE ACETIC ACID.—10 c.c. of glacial acetic acid with 25 c.c. water. Some prefer dilute nitric acid (1 : 5). If too much nitric acid be present, the lead sulphate is not completely separated.

[4] When very small amounts of lead are to be precipitated as sulphide, E. Murmann (*Monats.*, **19**, 404, 1899; U. Antony and T. Benelli, *Gazz. Chim. Ital.*, **26**, i, 218, 1896) adds mercuric chloride to the solution before passing the gas. This prevents any colloidal lead sulphide passing through the filter-paper. The mercuric sulphide is volatilised on roasting the precipitate.

[5] The presence of calcium chloride in a dilute solution of lead chloride in hydrochloric acid or nitric acid may inhibit the precipitation of lead sulphide owing to the solubility of lead sulphide in a solution of calcium chloride and acid. K. H. Mertens, *Pharm. Centr.*, **24**, 273, 1883; H. Hager and E. Geissler, *ib.*, **24**, 273, 1883.

[6] A. Gawalovski (*Zeit. anal. Chem.*, **26**, 51, 1887) suggests saturating the margin of the filter-paper with paraffin or fat (free from ash) in order to prevent the creeping of the precipitate over the edge of the paper.

[7] F. Moldenhauer (*Chem. Ztg.*, **22**, 256, 1898; *Chem. News*, **79**, 182, 1899) washes first with water and then with warm ammonium sulphide.

The precipitated mixture of zinc and lead sulphides is ignited in a porcelain crucible at a low temperature,[1] in order to burn off the filter-paper and volatilise the mercuric sulphide. Brush the residue into a small beaker and wash out the crucible with dilute nitric acid (1 : 5). Add about 5 c.c. of concentrated sulphuric acid and evaporate down to a volume of 3 c.c. Separate the lead sulphate as on page 326. Weigh the ignited precipitate of lead sulphate as $PbSO_4$ and add 0·0006 grm. The weight of the lead sulphate, multiplied by 0·85254, represents the weight of normal white lead—$2PbCO_3$. $Pb(OH)_2$—in the given sample. The zinc is precipitated from the cold filtrate as zinc ammonium phosphate (page 387), and the corresponding amount of ZnO or $ZnCO_3$ computed in the usual manner.

The Insoluble Portion.—Boil the residue with 20 c.c. dilute hydrochloric acid (1 : 1) and 5 grms. of ammonium chloride for 5 minutes. Dilute to 400 c.c. Boil 5 minutes. The lead and calcium sulphates are dissolved; barium sulphate,[2] silica and silicates remain undissolved. Filter and wash with hot water. The lead is precipitated from the filtrate by hydrogen sulphide.[3] The lead sulphide is treated as described above and reported as lead sulphate. The filtrate is treated with ammonia [4] and ammonium oxalate to precipitate the lime as calcium oxalate (page 202). Report as calcium sulphate. The residue (insoluble in ammonium chloride and hydrochloric acid), containing the barium sulphate, sand and clay, is ignited in a platinum crucible and weighed. Fuse the residue with ten times its weight of sodium carbonate. Extract with water, filter and wash. Digest the residue with dilute hydrochloric acid; filter; boil; add sulphuric acid to precipitate barium sulphate (page 582); weigh the precipitate and report as barium sulphate. Deduct this weight from the "insoluble" and report the difference as "clay, sand and insoluble silicates."

Collecting these results together, it will be seen that we have followed the subjoined scheme (on next page).

Carbon dioxide can be determined as indicated on page 625.

Water is determined as indicated on page 643 or 645.

Iron is determined by dissolving 5 grms. of the original sample in dilute nitric acid. Precipitate the lead as sulphate; filter; evaporate to dryness; dissolve the residue in 1 c.c. of hydrochloric acid and a little water; and make the solution up to 200 c.c. Determine the iron colorimetrically [5] (page 185) in 100 c.c.

Copper is determined colorimetrically by the ferrocyanide process (page 372) in the 100 c.c. remaining after the iron has been determined.

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[1] For the alleged volatilisation of lead sulphide, see H. Rose, *Pogg. Ann.*, 110, 134, 1860; G. F. Rodwell, *Journ. Chem. Soc.*, 15, 43, 1863; A. Souchay, *Zeit. anal. Chem.*, 4, 63, 1865; A. Classen, *Journ. prakt. Chem.*, (1), 96, 257, 1865.

[2] It must be remembered that heavy spar is slightly soluble in hydrochloric and nitric acids. Hence the "insoluble" heavy spar can only be determined approximately, unless the solution be evaporated to dryness and the residue taken up with water, filtered, washed and calcined at a low red heat. Note that the "total heavy spar" does not necessarily represent the amount of heavy spar added to the white lead, because the heavy spar used is not usually pure barium sulphate, but contains, say: 90 per cent. $BaSO_4$; 2 per cent. CaO; 7 per cent. SiO_2; 1 per cent. Al_2O_3 and Fe_2O_3. Since different solvents may dissolve different amounts of the heavy spar, it is easy to see how different "total insolubles" may be reported by different analysts. In exact work it is as well to fuse the "insoluble" with sodium carbonate as indicated in the text.

[3] For the precipitation of lead sulphide from hydrochloric acid solutions, the solution should not contain more than 2·5 or 3 c.c. of hydrochloric acid (sp. gr. 1·16) per 100 c.c. of solution.

[4] If alumina be precipitated when ammonia is added, filter, wash, ignite, weigh and report as alumina.

[5] A. Lecrenier, *Bull. Soc. chim. Belg.*, 18, 404, 1904; J. A. Schæffer, *Journ. Ind. Eng. Chem.*, 4, 659, 1912.

I. Soluble in dilute acetic acid. Treat with H_2S.
    A. Soluble. Add sulphuric acid.
       (a) Soluble. Add ammonium oxalate.
          1. Soluble. Add microcosmic salt.
             (i.) Soluble. Reject.
             (ii.) Insoluble Mg salt .   .   .   . $MgCO_3$.
          2. Insoluble Ca salt   .   .   . $CaCO_3$.
       (b) Insoluble barium sulphate   .   .   . $BaCO_3$.
    B. Insoluble. Take up with HNO_3, add H_2SO_4.
       (a) Soluble. Add microcosmic salt.
          1. Soluble. Reject.
          2. Insoluble Zn salt   .   .   .   .   ZnO or $ZnCO_3$.
       (b) Insoluble Pb salt .   .   .   .   . $2PbCO_3 . Pb(OH)_2$.
II. Insoluble. Digest with HCl and NH_4Cl.
    A. Soluble. Pass H_2S.
       (a) Soluble. Add ammonium oxalate.
          1. Soluble. Reject.
          2. Insoluble Ca salt   .   .   .   . $CaSO_4$.
       (b) Insoluble Pb salt .   .   .   .   . $PbSO_4$.
    B. Insoluble. Weigh, fuse sod. carb., etc.
       (a) Soluble. Add H_2SO_4.
          1. Soluble. Reject.
          2. Insoluble Ba salt .   .   .   . $BaSO_4$.
       (b) Insoluble. Subtract weight of II. B., (a) 2, from II. B., Insolubles.

Acetic acid is determined by alternate straight and steam distillation from a mixture of the sample with phosphoric acid.[1] The distillate is titrated with $0.1N$-NaOH and phenolphthalein as indicator until 10 c.c. of fresh distillate require but a drop of the alkaline solution to redden the indicator.

Soluble salts are isolated by boiling 5–10 grms. of the sample with 100 c.c. of water. Filter and wash. The sulphates are often determined by the barium chloride process (page 703). The barium sulphate may be expressed either in terms of SO_3, or, as is sometimes done, as $ZnSO_4$.

Sulphur dioxide or sulphites are sometimes found in the quick process white leads. Mix 2 grms. of the dried sample with 100 c.c. of recently boiled cold water in a 300 c.c. Erlenmeyer's flask; add 5 c.c. of concentrated sulphuric acid. Thoroughly agitate the mass. In about 15 minutes, titrate the mixture with $0.1N$-iodine solution, using starch as indicator. Continue the titration until the blue colour develops. 1 c.c. of $0.1N$-iodine solution represents 0.0032 grm. of SO_2.

§ 156. The Analysis of Red Lead and Litharge.

Red lead is usually made by roasting "pig lead" until oxidation ceases. The red lead may contain as impurities or adulterants heavy spar, lead sulphate, silica, ferric oxide, copper oxide and bismuth oxide. It also contains metallic lead and various lead oxides—PbO, Pb_2O_3, PbO_2. Silica and clay may be derived from the floor of the muffle in which the red lead was roasted. Owing to the difference in the specific gravity of heavy spar and red lead, good mixing is difficult and an intimate mixture is liable to segregate when travelling in casks. Hence samples drawn from different parts of the same cask may give different results. Care must therefore be exercised in the sampling.[2]

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[1] G. W. Thompson, *Journ. Soc. Chem. Ind.*, **24**, 587, 1905.
[2] For the analysis of red lead and litharge, see *Proc. Amer. Soc. Testing Materials*, **14** (1), 281, 1914; J. Milbauer and B. Pivnička, *Zeit. anal. Chem.*, **53**, 345, 1914; A. P. West, *Philippine J. Sci.*, **8**, 429, 1914; P. Beck, *Zeit. anal. Chem.*, **54**, 137, 1915; J. A. Schæffer, *Journ. Ind. Eng. Chem.*, **8**, 237, 1916; R. L. Hallows, *Glass Ind.*, **9**, 269, 1928; G. A. Ampt, *Proc. Soc. Chem. Ind. Victoria*, **30**, 353, 1930; N. Busvold, *Chem. Ztg.*, **56**, 106, 1932; G. Bruhns, *ib.*, **55**, 50, 1931; J. F. Sacher, *Farbe und Lack*, 403, 1933; S. Kettle, *Chemist-Analyst*, **25**, 6, 1936.

Dissolve, say, 10 grms. of the given sample in 10 per cent. nitric acid, or in acetic acid. The dissolution is greatly facilitated by the addition of about 10 c.c. of hydrogen peroxide (5 per cent.) [1] just after the addition of the nitric acid. Heat the solution for about an hour on the water bath. Filter and wash with hot water. The insoluble residue may contain clay, silica and heavy spar—barium sulphate.[2] This is treated as indicated for white lead (page 329). The filtrate is evaporated to dryness with nitric acid in order to make any silica in it insoluble and the latter is filtered off. The filtrate from the silica is treated with sulphuric acid in the usual way, in order to precipitate the lead as sulphate. Keep the excess of acid down to about 3 c.c. of concentrated sulphuric acid per 100 c.c. of solution. The filtrate from the lead sulphate is treated with hydrogen sulphide to precipitate the arsenic, antimony, copper and bismuth as sulphides. Separate the arsenic and antimony from the copper and bismuth by means of sodium monosulphide (page 276); determine the copper colorimetrically (page 372). If no arsenic or antimony be present, determine the copper in the filtrate from the lead.[3] Iron,[4] zinc and lime can be determined, if present, in the filtrate from the hydrogen sulphide precipitate (page 275).

Metallic Lead.—Red lead and litharge frequently contain free metallic lead diffused throughout the mass in fine granules—maybe up to 3 per cent.[5] To determine the amount, dissolve a known weight of the red lead in dilute acetic acid at 40° in the presence of hydrogen peroxide. Wash the residue with an acetic acid solution of ammonium acetate and then with water. Dry and weigh the residue. If other impurities be present, the metallic lead can generally be separated by treatment with dilute nitric acid, and either the washed residue dried and its weight subtracted from the original weight of the residue, or the lead determined in the nitric acid solution as usual.

Lead Monoxide.—The presence of lead monoxide, due to imperfect oxidation, is common. Transfer 1 grm. of the dried sample to a small beaker and digest for 30 minutes on a water bath with 25 to 30 c.c. of a neutral saturated solution of lead acetate, in which lead monoxide dissolves. It is advisable to cover the

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[1] Hydrogen peroxide of commerce sometimes contains sulphuric acid and in consequence may precipitate lead sulphate, hence pure hydrogen peroxide must be used. Cane sugar, oxalic acid (R. Fresenius, *Anleitung zur quantitativen Analyse*, Braunschweig, **2**, 484, 1903), tartaric acid (G. Torossian, *Journ. Ind. Eng. Chem.*, **8**, 1076, 1916), lactic acid (A. Partheil, *Chem. Ztg.*, **31**, 941, 1907), methyl alcohol, glycerol, formaldehyde, phenylhydrazine and hydroxylamine hydrochloride have also been suggested (E. Pieszczek, *Pharm. Ztg.*, **52**, 922, 1908; F. P. Dunnington, *Zeit. anal. Chem.*, **28**, 338, 1889; L. Opificius, *ib.*, **28**, 345, 1889; H. Schlossberg, *ib.*, **41**, 740, 1902), but hydrogen peroxide will be difficult to improve upon.

[2] Barium sulphate is not a common impurity of normal red lead, since it makes the lead incline to an orange tint. The heavy spar in "tinted red leads" may vary from 10 to 70 per cent. Highly adulterated red lead has been stained with aniline dyes to a good standard colour (M. Frehse, *Ann. Chim. anal. app.*, **11**, 176, 1906). The dye can be detected by the tint acquired by digesting the red lead in a suitable solvent. Shake 20 c.c. of 95 per cent. alcohol with 2 grms. of the sample, heat to boiling and let settle. Pour off the alcohol and boil with 20 c.c. of water; let settle and proceed in a similar way with ammonium hydroxide. If any of these three solvents has been coloured, the red lead is probably coloured with an organic dye.

[3] For the determination of copper, see T. B. Blunt, *Chem. News*, **32**, 3, 1875; P. Beck, *Zeit. anal. Chem.*, **54**, 137, 1915; C. R. Hardy, *Chem. News*, **120**, 256, 1920; H. Blumenthal, *Mitt. deut. Materialsprüfungsanstalt*, Sonderheft, **22**, 40, 1933. For bismuth, see P. Beck, *loc. cit.*; H. Heinrichs and M. Hertrich, *Glastech. Ber.*, **2**, 112, 1924.

[4] For the determination of iron, see P. Beck, *loc. cit.*; C. R. Hardy, *loc. cit.*; H. Heinrichs and M. Hertrich, *loc. cit.*; J. F. Sacher, *Farben Ztg.*, **31**, 2131, 1926; L. Springer, *Glastech. Ber.*, **4**, 458, 1927; H. Heinrichs, *Zeit. angew. Chem.*, **41**, 450, 1928; T. B. Blunt, *loc. cit.*

[5] G. C. Wittstein, *Dingler's Journ.*, **194**, 84, 1869; *Chem. News*, **20**, 249, 1869; P. Fluch, *Zeit. anal. Chem.*, **75**, 371, 1928; T. B. Blunt, *Chem. News*, **32**, 3, 1875.

beaker with a watch-glass. Filter off the insoluble red lead on a weighed Gooch crucible. Wash and dry at 100° to constant weight.[1] Report the loss in weight as lead monoxide.

Lead Peroxide.—Digest, say, one gram of dry red lead in a porcelain dish with 20–30 c.c. of dilute nitric acid (1 : 5) on a water bath for a few minutes,[2] when insoluble lead dioxide [3] and soluble lead nitrate are formed. The former may be filtered off, washed, dried at 110°, and weighed. For the volumetric determination, add 50 c.c. of 0·2N-oxalic acid to the weighed quantity of red lead and heat to boiling.[4] Titrate the excess of oxalic acid in the hot solution without filtering by means of a 0·2N-potassium permanganate solution. If 39 c.c. of permanganate are used, then $50 - 39 = 11$ c.c. of 0·2N-oxalic acid are used for the reduction of the gram of red lead. From the equation

$$PbO_2 + H_2C_2O_4 = PbO + H_2O + 2CO_2$$

it follows that 1000 c.c. of the 0·2N-oxalic acid represents 23·92 grms. of PbO_2, or 1 c.c. represents 0·02392 grm. of PbO_2. Hence 11 c.c. of oxalic acid correspond with $11 \times 0.02392 = 0.2631$ grm. PbO_2. Hence one gram red lead has 0·2631 grm. PbO_2, or 26·31 per cent. PbO_2.[5] The lead sesquioxide may be calculated from the total weight of lead in the sample less that present as free lead, PbO and PbO_2.

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[1] Lead sesquioxide—Pb_2O_3—is scarcely attacked by the lead acetate—E. E. Dunlap, *Journ. Amer. Chem. Soc.*, **30**, 611, 1908; L. Opificius, *Chem. Ztg.*, **12**, 477, 1888. D. Woodman (*Journ. Amer. Chem. Soc.*, **19**, 339, 1897), using this process, found a variation of 41–92 per cent. in the amount of red lead, and from 8–59 per cent. of lead monoxide, in commercial red leads on the American market. J. Lowe (*Dingler's Journ.*, **271**, 472, 1889) recommends lead nitrate. J. Milbauer (*Chem. Ztg.*, **38**, 477, 1914) concentrated potassium hydroxide or lead acetate.

[2] F. Lux, *Zeit. anal. Chem.*, **19**, 153, 1880; E. Rupp, *ib.*, **42**, 732, 1903; H. Schlossberg, *ib.*, **41**, 735, 1902; P. Beck, *ib.*, **47**, 465, 1908; H. Fleck, *Ber.*, **20**, 855, 1881; W. P. Joshua, *Analytische Beiträge zur Bestimmung von Bleisuperoxyd neben Blei und Bleioxyd*, Zürich, 1906; A. Chevala and H. Colle, *Gazz. Chim. Ital.*, **41**, ii, 551, 1911; *Zeit. anal. Chem.*, **50**, 209, 1911; J. F. Sacher, *Chem. Ztg.*, **35**, 731, 1911; J. A. Schæffer, *Journ. Ind. Eng. Chem.*, **8**, 237, 1916; A. Ipiens, *Zeit. anal. Chem.*, **53**, 261, 1914; J. Milbauer and B. Pivnička, *ib.*, **53**, 345, 569, 1914; E. Szterkhers, *Ann. Chim. anal. app.*, **7**, 214, 1902; L. Moser, *Chem. Ztg.*, **39**, 245, 1915. C. Finzi and E. Rapuzzi (*Zeit. anal. Chem.*, **52**, 358, 1913) treat the peroxide with hydrazine acetate and compute the amount of lead peroxide from the volume of nitrogen evolved. *Cf.* E. Schurmann and K. Charsius, *Chem. Ztg.*, **58**, 55, 1934; *Mitt. deut. Materials-prüfungsanstalt, Sonderheft*, **22**, 37, 1933. A. Masselin and A. Caille, *Bull. Soc. ind. Rouen*, **60**, 99, 1932.

[3] It is simply a *façon de parler* to say "the PbO_2 content of red lead," since this statement does not imply the existence of PbO_2 in red lead. Red lead is probably not a mixture of PbO_2 and $2PbO$. See J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, London, **7**, 676, 1927. For the determination of free lead peroxide in litharge, see L. S. Dean, *Chem. News*, **111**, 2, 1915; W. V. Morgan, *Journ. Ind. Eng. Chem.*, **11**, 1055, 1919.

[4] Impurities like sand, barium sulphate, lead sulphate, remain undissolved.

[5] G. Topf (*Zeit. anal. Chem.*, **26**, 296, 1887; W. Diehl, *Dingler's Journ.*, **246**, 196, 1882) heats the red lead with hydrochloric acid and marble, and passes the chlorine evolved into a standard solution of potassium iodide (5 grms. neutral KI, free from iodates, in 100 c.c. of water) contained in each of a couple of Péligot's tubes, and determines the liberated iodine in the regular way, p. 285. V. Farsoe, *Zeit. anal. Chem.*, **46**, 308, 1907; A. Travers, *Compt. rend.*, **196**, 548, 1933. After the action, the iodine solution is titrated with 0·1N-sodium arsenite. In a sample weighing 0·3624 grm., 10 c.c. of the 0·1N-sodium arsenite solution were needed. Hence the red lead contained 33·0 per cent. of PbO_2. C. Marchese (*Gazz. Chim. Ital.*, **37**, ii, 289, 1907) has examined several methods of determining lead peroxide in red lead—H. Forestier's method (*Zeit. angew. Chem.*, **11**, 176, 1898; *Annal. Lab. Chim. R. Gabelle*, **5**, ii, 486, 1906), in which the red lead is heated for half an hour on a water bath with 10 c.c. of 10 per cent. acetic acid solution, and 20 c.c. of water. The insoluble residue after washing represents "lead peroxide and other insoluble matter."—E. Szterkhers' method (*Ann. Chim. anal. app.*, **7**, 214, 1902) depending on the insolubility of lead peroxide in dilute

In the gravimetric determination of lead peroxide, the sample is digested with warm dilute nitric acid (1 : 5) and allowed to stand in a cool place for 24 hours. Filter through a Gooch crucible, wash with hot water, dry 6 hours between 105° and 110° and weigh as PbO_2. To calculate the corresponding amount of Pb_3O_4 multiply by 2·8662. The difference between this weight and the weight of the original sample does not represent the litharge in the sample, because lead sesquioxide—Pb_2O_3—dissolves in the nitric acid and would be in consequence reported as litharge. In calculating the PbO_2 to Pb_3O_4, allowance must be made for any insoluble residue in the sample (page 331).

§ 157. The Analysis of Lead Chromates.

The chrome yellows and chrome reds are lead chromates or basic lead chromates with more or less lead sulphate, white lead, lead oxide, barium sulphate, calcium carbonate, calcium sulphate, zinc oxide, ferric oxide and silica, along with soluble salts due to imperfect washing, e.g. potassium sulphate, potassium dichromate, potassium permanganate. A chrome yellow may be considered adulterated if it contains anything besides insoluble lead chromates and lead compounds. The scheme of analysis depends upon the information desired.[1]

Insoluble Matter.- Digest 1 grm. of the dry powder (100's lawn) in boiling concentrated hydrochloric acid, adding half a dozen drops of alcohol to the boiling liquid one at a time. This accelerates the dissolution of the lead chromates. Lead chloride — $PbCl_2$ — and chromic chloride—$CrCl_3$—are formed. Evaporate the solution to dryness. Add a few drops of hydrochloric acid and 100 c.c. of hot water. Filter the hot solution (a hot-water funnel,[2] fig. 90, is here useful).
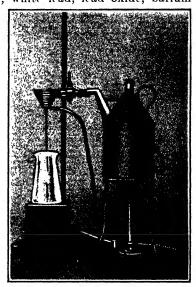
FIG. 90.—Hot Funnel.

nitric acid—2 c.c. of acid (sp. gr. 1·18) and 30 c.c. of water—free from nitrous acid. Forestier's method requires a longer heating or stronger acid than is prescribed by its author. Topf's and Szterkhers' methods are considered best. A. Partheil (*Ver. Ges. deut. Naturforsch. Aertze*, 159, 1907) prefers Topf's process. See also H. Blumenthal, *Mitt. deut. Materials-prüfungsanstalt, Sonderheft*, 22, 40, 1933; A. V. Pamfilov, *Zeit. anal. Chem.*, 78, 40, 1929; A. V. Pamfilov and E. G. Ivancheva, *ib.*, 79, 186, 1930; 88, 23, 1932; *Journ. Gen. Chem.* (*U.S.S.R.*), 1, 760, 1931; 3, 262, 1933.

[1] E. F. Scherubel and E. S. Wood, *Journ. Ind. Eng. Chem.*, 2, 482, 1910; P. H. Walker, *Bull. U.S. Dept. Agric. Chem.*, 109, 29, 1910; M. Lachaud and C. Lapierre, *Bull. Soc. chim.*, (3), 6, 335, 1891; *Compt. rend.*, 110, 1035, 1890; A. Voet and W. Oostveen, *Ind. Chim. Belge*, 7, 239, 1936.

[2] HOT FUNNEL.—There are numerous types of hot funnel very useful for filtering hot solutions which have a tendency to crystallise on cooling. In filtering saturated salt solutions liable to crystallise, it is best to use funnels with the stem cut off, e.g. Gattermann's funnel. A good temporary hot-water jacket can be made by wrapping a piece of flexible copper, lead or "compo" gas piping spirally two or three times round the funnel and blowing steam through the spiral by connecting the pipe with a tin can containing boiling water, fig. 90 (A. Horvath, *Liebig's Ann.*, 171, 135, 1874; O. von Liebreich, *Chem. Ztg.*, 11, 153, 1887; *Zeit. anal. Chem.*, 27, 387, 1888; 24, 582, 1885; V. Brudny, *Zeit. Mikros.*, 26, 418, 1910). Another simple form is a plain sheet zinc or copper bath with a sheet zinc or copper funnel soldered

Wash the residue with hot water,[1] ignite and weigh. The result is sometimes reported as "insoluble matter"; it contains barium sulphate and silica. The silica can be volatilised by treatment with hydrofluoric acid and sulphuric acid (page 149). The residue is then reported as "barium sulphate," and the loss in weight by the hydrofluoric acid treatment is reported as "silica."[2]

Calcium Sulphate.—Add a hot solution of barium chloride to the boiling filtrate, and determine the sulphates in solution as barium sulphate (page 703). Calculate the corresponding amount of calcium sulphate by multiplying the weight of the barium sulphate by 0·5832.

Zinc Oxide and Calcium Carbonate.—Digest a gram of the sample with concentrated acetic acid, boil, dilute to 100 c.c., filter and wash with dilute acetic acid. The zinc oxide, the calcium salts and some lead oxide pass into solution. Precipitate the lead and zinc by means of hydrogen sulphide, filter and wash as described on page 328. Add ammonia to the filtrate until the solution is alkaline; precipitate the lime as calcium oxalate and proceed as described on page 202. The weight of the calcium oxide so obtained, multiplied by 1·7846, represents the corresponding amount of calcium carbonate. The weight of the calcium sulphate obtained in the preceding determination, multiplied by 0·7351, gives the equivalent amount of calcium carbonate. The difference in the two results represents the amount of calcium carbonate in the given sample.

The mixed lead and zinc sulphides are treated as described on page 329, but the lead sulphate is rejected. The zinc is weighed as phosphate, page 387, and reported as zinc oxide.

Ferric Oxide and Lead Chromate.—Boil 1 grm. of the powdered sample with about 10 grms. of potassium hydroxide and 100 c.c. of water, filter and wash with hot water. The alkaline filtrate containing the lead chromate in solution [3] is acidified with acetic acid, when insoluble lead chromate will be precipitated. This is collected on a weighed Gooch crucible, washed with water, dried at 110° and weighed as lead chromate — $PbCrO_4$.

The filter-paper contains the ferric oxide, barium sulphate, silica and lead oxide. Ignite the mixture slowly, and at as low a heat as possible, in a porcelain crucible so as to prevent the mass sticking to the sides of the crucible. Digest the residue with 5 c.c. of hot concentrated hydrochloric acid until the residue is colourless, then transfer the mixture to a beaker with 50 c.c. of water. Filter off the insoluble silica and barium sulphate. Nearly neutralise the filtrate with ammonia and precipitate the lead as lead sulphide. Wash and reject the precipitate. The filtrate is boiled to expel the hydrogen sulphide and

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into the bath, so that the glass funnel fits into the metal funnel, with the stem of the glass funnel below the bath. If necessary, the bath can be fitted with a condenser or with a constant level attachment. In Paul's steam-heated funnel (T. Paul, *Ber.*, **25**, 2208, 1886) the steam is blown through a copper tube bent in a spiral form to fit the funnel. The condensed steam returns to the boiler. A simple method of heating by an electric current is also available.

[1] If lead sulphate be present, it must now be washed out by digesting the residue, before ignition, with sodium thiosulphate, or ammonium acetate, or ammonium chloride, and precipitated from the filtrate by treatment with hydrogen sulphide (page 275). If the residue be coloured, repeat the digestion with a few drops of hydrochloric acid. Some basic lead chromates may be present, which dissolve very slowly in acids; in that case, the addition of alcohol or hydrogen peroxide is advisable to hasten the process of dissolution.

[2] There are objections to this practice. Lead sulphate, if it be present, would thus be reported as barium sulphate. For a more exact method of treating the insoluble residue, see white lead, page 329.

[3] A. Voet and W. Oostveen (*Ind. Chim. Belge*, **7**, 239, 1936) pour the alkaline solution into excess of dilute hydrochloric acid, cool, add excess of potassium iodide and titrate the liberated iodine with thiosulphate.

treated with a few drops of nitric acid to oxidise the iron. The iron is precipitated with ammonia, washed, ignited and weighed as ferric oxide (page 164).

Total Lead Oxide.—1 gram of the sample is digested with concentrated hydrochloric acid, evaporated to dryness and the residue treated with a few drops of hydrochloric acid and about 100 c.c. of hot water. Boil the solution until it has a clear green colour. Filter. Add 5 to 10 grms. of sodium acetate to replace the free hydrochloric acid by acetic acid.[1] Add 5 c.c. of acetic acid and a gram of potassium chromate. Stir the solution vigorously. The lead chromate is precipitated. Filter through a weighed Gooch crucible, wash the precipitate with water, dry at 110° and weigh as lead chromate—$PbCrO_4$.[2] The difference in the weight of the lead chromate so determined and that previously obtained is multiplied by 0·6905, and the result reported as lead monoxide—PbO.

White Lead.—If white lead be present, determine the amount of carbon dioxide in the given sample (page 624 or 625), and deduct the carbon dioxide corresponding with the calcium carbonate previously determined. The result, multiplied by 8·8144, gives the corresponding amount of white lead—$Pb(OH)_2$. $2PbCO_3$. The amount of white lead is multiplied by 0·8633 to get the corresponding amount of lead oxide—PbO. This is deducted from the lead oxide previously obtained.

Soluble Salts.—The soluble salts—acetates, dichromates, sulphates, nitrates—present are generally derived from imperfect washing in the manufacture of the chromate. The soluble salts are determined by weighing, say, 5 grms. of the dry (109°) impalpable powder in a Gooch crucible (dried at 109°), and washing six times with 25 c.c. of cold water. Dry the contents of the crucible at 109° and weigh. The loss in weight represents the soluble salts removed by the water. The washings may be examined, if desired, and the salts just named specially determined qualitatively, or quantitatively.[3]

Results.—Scherubel and Wood's test analysis on a known mixture gave the following percentage results:—

	SiO_2.	$BaSO_4$.	Fe_2O_3.	$CaSO_4$.	ZnO.	$CaCO_3$.	$PbCrO_4$.	PbO.
Used	4·76	4·76	4·76	4·76	9·52	4·76	57·14	9·54
Found	4·52	4·70	4·88	4·90	9·54	4·64	57·04	9·68

These results must be considered satisfactory for technical work.

Naples Yellow.—In evaluating this substance, lead and antimony are to be separated. Determine the antimony volumetrically in an aliquot portion of the solution: the lead may be determined by precipitation as sulphide by hydrogen

[1] If iron be present, the solution turns reddish-brown.

[2] The separation of lead as chromate is sometimes advantageous under conditions where the sulphate, sulphite or molybdate separations would be less convenient. This, for instance, is the case in separating small quantities of lead from copper and zinc in acetic acid solutions, and in separating lead from silver in ammoniacal solutions. If bismuth be present, some bismuth chromate will be precipitated with the lead chromate, and the two must be separated by other methods—W. Diehl, *Chem. Ind.*, 6, 157, 1883. Compare H. Funk and J. Weinzierl, *Zeit. anal. Chem.*, 81, 380, 1930. For the solubility of lead chromate in water, see M. Huybrechts and C. Degard, *Bull. Soc. chim. Belg.*, 42, 331, 1933. Several volumetric processes are based on this reaction. An excess of a standard solution of potassium dichromate is added to the solution of the lead salt and the excess determined by a standard solution of ferrous iron. A. Longi and L. Bonavia, *Gazz. Chim. Ital.*, 26, i, 327, 1896; G. Giorgis, *ib.*, 26, ii, 554, 1896; R. K. Meade, *Journ. Amer. Chem. Soc.*, 19, 374, 1897; J. H. Wainwright, *ib.*, 19, 389, 1897; C. W. Simmons, J. R. Gordon and H. C. Boehmer, *Canad. Chem. Journ.*, 4, 139, 1920; I. M. Kolthoff, *Pharm. Weekblad*, 57, 934, 1920; W. W. Scott, *Ind. Eng. Chem.*, 17, 678, 1925; Z. Karaoglanov and B. Sagortschev, *Zeit. anal. Chem.*, 81, 275, 1930.

[3] In this case probably more powder will be needed.

sulphide in an alkaline solution, hot, if necessary, to keep the lead chloride in solution.[1]

§ 158. The Determination of Silver in Lead Compounds by the Turbidity Method.

Silver in small quantities is best determined by cupellation. The amount present in red or white lead is usually too small to be determined satisfactorily by other gravimetric[2] or volumetric processes. Blunt[3] determines the silver by the following turbidity process:—Dissolve 10 grms. of, say, red lead in 50 c.c. of dilute nitric acid (sp. gr. 1·42, 1 vol.; water 3 vols.) quite free from chlorides. Dilute to 120 c.c.; filter; wash the residue with a little distilled water; make the filtrate up to 200 c.c. Pipette out 100 c.c. of the solution, add one drop of concentrated hydrochloric acid and stir. The lead chloride passes into solution and the silver chloride produces a white turbidity. Allow to stand for an hour and then filter through a dry 5·5 cm. filter-paper into the right hand test glass of a colorimeter. The remaining 100 c.c. of solution is placed in the left hand test glass and similarly treated with one drop of acid and stirred. Add a standard solution of silver nitrate[4] drop by drop with constant stirring to the solution in the right hand test glass until the turbidity in both vessels appears the same. The volume of the silver nitrate solution used represents the amount of silver in 100 c.c. of the solution. *Cf.* page 749.

§ 159. The Determination of Silver and Gold by Cupellation.

This process is very old, and an enormous number of determinations of gold and silver by this process are made daily in assay offices in different parts of the world. A known weight of the lead compound is reduced to the metal. The metal is then heated in a shallow cup, called a *cupel*, made of bone ash or some other suitable material, whereby the lead is oxidised and absorbed by the cupel; the silver remains behind as a small bead. The silver will be alloyed with gold, if gold be present.[5]

Roasting and Fusion.—The object of the fusion is to collect the silver in a button of metallic lead-silver alloy. Intimately mix 100–120 grms. of pure, dry litharge, red lead or white lead and, say, 10 grms. of the finely powdered lead ore with the flux—sodium bicarbonate 60 grms., argol 2 grms.—on a sheet of glazed paper. The mixture is transferred to a fireclay crucible so as to fill the crucible not more than three-quarters full,[6] and the whole contents covered with a layer of finely powdered dry borax glass. The lid is placed on the crucible and the whole heated gradually to prevent breaking the crucible or prevent the charge from "blowing." When the contents of the crucible have ceased bubbling and all is in a state of quiet fusion, the crucible is removed from the fire and gently tapped, sides and bottom, in order to assist the molten metal inside to collect on the bottom of the crucible. The molten contents of the crucible are usually poured into conical iron moulds; or the crucible

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[1] The lead may also be precipitated as oxalate and the lead oxalate determined by titration with potassium permanganate, as indicated for lime (page 205).

[2] Precipitation as silver chloride or iodide.

[3] T. P. Blunt, *Chem. News.*, **32**, 3, 1875; J. Krutwig, *Ber.*, **15**, 307, 1264, 1882; G. Rebière, *Bull. Soc. chim.*, (4), **17**, 306, 1915; T. von Heidlberg, *Biochem. Zeit.*, **192**, 238, 1928.

[4] SILVER NITRATE SOLUTION.—Dissolve 1·5748 grms. silver nitrate in water and make the solution up to a litre. 1 c.c. represents 0·001 grm. of silver—Ag.

[5] For a critical examination of the cupellation process, see J. W. A. H. Smit, *Rec. Trav. chim.*, **40**, 119, 1921.

[6] Say, a Battersea round, approximately size E.

may be allowed to cool and then broken. The slag is separated from the lead button by hammering the button on an anvil into a cube with its corners flattened.[1] The button should weigh about 20 grms. If it weighs more, use less argol; if less, more argol.

Cupellation.—The object of the cupellation is to remove the "base" metals by oxidation and absorption in the cupel. The "noble" metals—gold and silver—remain on the cupel bottom after the operation in the form of a small bead. Place three or four empty cupels [2] in a red-hot muffle.[3] In about 10 minutes the button of lead is placed by means of the "cupel tongs" in the centre of a hot cupel free from cracks. Close the door of the muffle. The lead melts (327°); a black scum develops on its surface. This disappears in a few minutes (about 675°) and the molten lead has a bright silvery appearance. The door of the muffle should be opened, but not wide enough to allow cold air to impinge directly on the cupel. Oxidation now sets in vigorously. The flakes of oxide which form on the surface of the button slide down its convex surface and are absorbed by the cupel. The temperature of the cupel should not exceed 750°—a temperature well below the melting-point of litharge (about 900°).

The most common mistake at this stage is too high a temperature. If the temperature of the muffle is right, "feathers" of litharge appear on the side of the cupel, nearest the doors of the muffle, and on the upper rim of the cupel. If the temperature is too low, feathers form low down in the cupel. If the muffle be not hot enough, put a lump of charcoal in front of the cupel. This will raise the temperature a little.

Sometimes the action stops during cupellation and the button solidifies. This is called "freezing." This arises when the lead has been oxidising more rapidly than the lead oxide has been absorbed by the cupel. In that case add more lead to the cupel. If "freezing" be due to the low temperature of the muffle, the temperature of the latter must be raised a little. The result of a cupellation with a button which has frozen is to be regarded with suspicion.

Traces of foreign metals—*e.g.* copper, antimony, iron, zinc—are partly absorbed by the cupel and partly volatilised as oxides. As the absorption of lead continues, the button becomes more and more spherical. At this stage the temperature of the muffle should be raised or the cupel pushed into a hotter part of the muffle. When the last of the lead has gone, the button appears to revolve axially in the cupel and it also seems to be covered with an iridescent film. The colours then disappear; the bead becomes dull and acquires a silvery tinge. If the temperature of the muffle be below the melting-point of the button (962° for silver) or if the cupel be withdrawn from the muffle, the bead suddenly becomes very bright—"flashing." Close the doors of the muffle for one or two minutes so as to remove the last traces of lead.

The cupel containing the bead is covered by placing another hot, empty cupel over it and both are then removed from the muffle. The object is to ensure slow cooling in order to prevent "sprouting" caused by the evolution of occluded oxygen by the silver bead. If the bead should sprout, start again. When cold, the bead is removed with a pair of forceps. If the bead be

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[1] If portions of lead or pasty-looking masses adhere to the sides of the crucible, the fusion is defective, and another fusion must be made.

[2] The success of the work is largely dependent on the quality of the cupel. If many cupels are required, they can be made with good bone ash in "cupel moulds"; if but few determinations are to be made, old and dry cupels of good quality can be purchased from the dealers. A good cupel will absorb its own weight of lead oxide. The cupel should be nearly twice as heavy as the lead button.

[3] That is varying from "red" to "bright red." Not "dull red," nor "white."

excessively small, merely touching it with a wet pin and lifting it on a watch-glass will suffice.   Dry the bead by warming and weigh.[1]   The bead should be examined with a lens before weighing to make sure that no particles of bone ash adhere to it.   If the bead is so contaminated, hold it in the "bead forceps," and brush it clean with a hard brush—"button brush."

The bead contains both gold and silver.   If the bead is white, it contains more than half its weight of silver; if yellow or reddish-yellow, it has about three-quarters of its weight of gold.   Intermediate tints represent different proportions of gold and silver.   For the determination of the amount of gold in the bead, see page 470.   In the case of red and white leads, if the silver be determined at all, it will usually suffice to report the weight of the bead as "silver."

§ 160. The Analysis of Galena.

Native galena—PbS—may be accompanied by products of the decomposition of lead sulphide—anglesite and cerussite—quartz, silicates, blende, calcite, fluorspar, heavy spar and pyrites.   Certain varieties also contain arsenic and antimony; and argentiferous galena may contain up to 1·0 per cent. of silver.

Decomposition of the Galena.—Moisten, say, half a gram of the finely powdered sample in a 250 c.c. basin with dilute nitric acid; and, after the cold mixture has stood for a few minutes, digest on the water bath with 15 c.c. of concentrated nitric acid.   The basin is covered by a clock-glass during the reaction to prevent loss by spurting.   When the violence of the action is over, evaporate the mixture to dryness on the water bath.[2]   Add 10 c.c. more of concentrated nitric acid, some water and 10–15 drops of bromine.   Heat the mixture with frequent stirring on the water bath, so as to complete the oxidation of the sulphide.   To decompose the bromates, add more nitric acid and evaporate to dryness.   Repeat this operation in all three times.   Boil the dry residue with 60 c.c. of water and 20 c.c. of concentrated hydrochloric acid so as to dissolve the lead sulphate.   Filter off [3] the residual gangue; wash well with boiling water.   If desired, the residue may be ignited, weighed and reported as "insoluble gangue."   This may contain the quartz, insoluble silicates, some silver chloride and the greater part of the barium sulphate.[4]

Transformation of the Decomposition Products into Sulphates.—Add 10 c.c. of dilute sulphuric acid (1 : 1) to the filtrate (or an aliquot portion of the filtrate) from the insoluble gangue, and evaporate the mixture until copious white fumes of sulphuric acid appear.   The evaporation should be carried nearly to

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[1] If the bead of silver be too small to weigh, its diameter can be measured with the microscope.   Suppose the bead has a diameter 0·18 mm.   The measurement is supposed to be the average of measurements in two or three different directions.   The volume of the bead is $0.5236 \times (0.18)^3$ cub. mm.   If the specific gravity of the silver be 10·5, the bead of silver will weigh $10.5 \times 0.5236 \times (0.18)^3 = 0.032$ mgrm. or 0·000032 grm.   V. Goldschmidt, *Zeit. anal. Chem.*, 17, 142, 1878; 16, 434, 1877; C. F. Föhr, *ib.*, 22, 195, 1883; *Chem. News*, 50, 114, 1884; G. Tate, *ib.*, 61, 43, 54, 1890; C. A. Gozdorf, *ib.*, 54, 231, 1886; D. Forbes, *ib.*, 15, 231, 1867; G. A. Goyder, *ib.*, 70, 194, 203, 1894; J. W. Richards, *Journ. Amer. Chem. Soc.*, 23, 203, 1901: J. S. Curtis, *Berg. Hütt. Ztg.*, 47, 3, 1888; M. Guerreau, *Bull. Soc. chim.*, (3), 27, 1902; *Chem. News*, 86, 194, 1902; J. I. Blair, *Min. Sci. Press*, 109, 526, 1914.

[2] A little hydrochloric acid generally aids the dissolution of the galena by dissolving the film of lead nitrate, which is almost insoluble in the strong acid and thus protects the galena from further attack.

[3] If lead only is to be determined by a volumetric process, this filtration may be omitted.

[4] The difference in weight after treatment with hydrofluoric acid will give the silica.   Fusion with sodium carbonate and extraction with water will give an insoluble residue of the carbonates.   These can be dissolved in nitric acid, the silver precipitated with hydrochloric acid and the barium with sulphuric acid (pages 582 and 748).   The total silver may be determined by cupellation.

dryness (3 c.c.) in order to ensure complete conversion of the lead salts into sulphates, to prevent too large an excess of acid and to drive off the nitric and hydrochloric acids. Let the mixture cool.

Separation of the Lead Sulphate.—Gradually add 100 c.c. of cold water and boil the mixture so as to dissolve the ferric and other soluble sulphates. The lead sulphate remains behind. If the lead sulphate is to be determined gravimetrically, filter the solution through a Gooch or Monroe crucible and complete the determination as indicated on page 326. If the lead is to be determined volumetrically, decant the clear liquid through a filter-paper, and wash by decantation with dilute sulphuric acid—about $1 \cdot 0 N\text{-}H_2SO_4$. Keep as much solid in the beaker as possible. Wash the paper with alcohol to remove sulphuric acid. Dissolve the precipitate on the paper by pouring a hot concentrated solution of ammonium acetate, slightly acidulated with acetic acid, through the filter-paper into the beaker containing the remainder of the lead sulphate. The amount of lead in the ammonium acetate solution can then be determined by the molybdate volumetric process (page 343). Low results by this process can often be traced to imperfect solution of the lead sulphate on the filter-paper.

Determination of Other Constituents.—Copper, antimony and arsenic can be precipitated as sulphides from the filtrate, and the copper separated from the antimony and arsenic, as indicated on page 276. The copper can be determined as indicated on page 367; the antimony and arsenic determined as indicated on page 308. The filtrate is boiled to drive off the hydrogen sulphide, oxidised with a few drops of hydrogen peroxide, and heated to boiling with an excess of ammonium chloride and a slight excess of ammonia. The precipitate is treated as indicated on page 164. Zinc, if present, will be found in the filtrate and determined as indicated on page 387. The sulphur can be determined by oxidising the powdered sample with nitric acid and bromine, and finally weighed as barium sulphate (page 703).

Other Methods of "Opening" Galena.—Other methods of decomposition are sometimes useful alternatives. Galena, for example, can be reduced to metallic lead [1] by fusing in a crucible a mixture of, say, 10 grms. with 75 grms. of potassium cyanide, beneath a layer of 12 grms. of powdered anhydrous borax. Cover the crucible with a lid and heat the mixture to redness until the reduction is complete (page 268). The metallic button is washed free from cyanide, dissolved in dilute nitric acid (1 : 5), and treated for lead by the sulphuric acid process (page 326).

The sodium peroxide fusion (page 264) is often most convenient for the determination of sulphur; and the process indicated in footnote 1, page 336, enables a determination of the lead to be made very quickly.[2]

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[1] A. W. Warwick, *Chem. News*, 63, 30, 145, 1891; F. Jean, *Bull. Soc. chim.*, (3), 9, 253, 1893.

[2] R. Benedict (*Chem. Ztg.*, 16, 43, 1896) decomposes galena by digestion with hydriodic acid (sp. gr. 1·7). Subsequent digestion with nitric acid transforms the lead iodide into nitrate, and the lead is then precipitated as sulphate. According to F. H. Storer (*Chem. News*, 21, 137, 1870; A. Mascazzini, *Zeit. anal. Chem.*, 10, 491, 1871; F. Mohr, *ib.*, 12, 142, 1873; F. Stolba, *Journ. prakt. Chem.*, (1), 101, 150, 1867), galena is reduced rapidly and completely by dilute hydrochloric acid (1 : 4) in contact with metallic zinc. Besides galena, metallic lead may be precipitated quickly and completely from the sulphate, nitrate, chromate, oxide, carbonate and chloride. The clear liquid decanted from the residue shows no trace of lead with hydrogen sulphide. C. Boucher (*Bull. Soc. chim.*, (3), 30, 933, 1903; *Chem. News*, 89, 56, 1904) attacks pyrites and galena by heating the powdered mineral intimately mixed with 4 to 5 times its weight of a mixture of 3 parts of sodium persulphate with 1 of ammonium nitrate in a dish or flask on a sand bath. For other methods of analysing galena, see J. A. Müller, *Bull. Soc. chim.*, (3), 31, 1303, 1904; *Chem. News*, 92, 15, 1905; P. Jannasch and

§ 161. The " Government Test " for the Solubility of Lead Frits.

The directions given in the *Home Office Circular*[1] for this test are as follows:—

"No glaze into the composition of which the fritted lead enters shall be regarded as satisfying the requirement as to insolubility which yields to a dilute solution of hydrochloric acid more than 2 per cent. of its dry weight of a soluble lead compound calculated as lead monoxide, when determined in the following manner:—A weighed quantity of dried material is to be continuously shaken for one hour, at the common room temperature, with 1000 times its weight of an aqueous solution of hydrochloric acid containing 0·25 per cent. of HCl. This solution is thereafter to be allowed to stand for one hour and to be passed through a filter. The lead salt contained in an aliquot portion of the filtrate is then to be precipitated as lead sulphide and weighed as lead sulphate."

The directions here are incomplete. It is difficult, indeed impossible, to filter some glazes satisfactorily through filter-paper, and if some silica passes
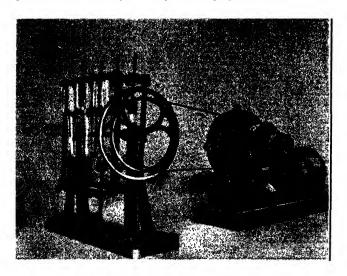
FIG. 91.—Shaking Apparatus.

into solution, it may, later on, be precipitated with the lead sulphide. Hence, dry the glaze at 100°.[2] Transfer, say, 0·5 grm. of the powder into a 500 c.c. Stohmann's shaking bottle closed with a rubber stopper, and fill the bottle up to the mark on the neck[3] with 0·25 per cent. hydrochloric acid. Shake the mixture for an hour in, say, Wagner's shaker, fig. 91. Let the bottle stand for

H. Kammerer, *ib.*, **72**, 78, 1895; *Ber.*, **28**, 1409, 1895; J. K. Meade, *Journ. Amer. Chem. Soc.*, **19**, 374, 1897; *Chem. Eng.*, **11**, 49, 1910; *Chem. News*, **101**, 137, 1910; W. Stahl, *Berg. Hütt. Ztg.*, **48**, 237, 1889.

[1] K. E. Digby, *Home Office Circular*, Dec. 14, 1889; Aug. 2, 1900; *Report of the Departmental Committee appointed to inquire into the Dangers attendant on the use of Lead in the manufacture of Earthenware and China*, London, 24, 1910.

[2] If a slop glaze be supplied, it must be thoroughly agitated and a portion evaporated to dryness, and the dry powder thoroughly mixed. Special attention is here needed, because the glaze is not usually homogeneous after it has been dried in a basin on the water bath.

[3] 500 grms., or 499·8 c.c. of 0·25 per cent. acid at 15°. The method in the text is sufficiently exact. 68·5 c.c. of 1·0N-HCl or 6·83 c.c. of the concentrated acid (sp. gr. 1·16) diluted to a litre will give a 0·25 per cent. solution.

one hour. Filter off a convenient quantity, say 425 c.c., of the clear solution, rejecting the first 10 c.c. which pass through the paper. Evaporate to dryness on a water bath. Take up the residue with dilute hydrochloric acid, so that the solution is but slightly acid (page 275). Filter and wash the silica. Add 1 c.c. of a saturated solution of mercuric chloride (page 328). The mercury may be ignored, because it is volatilised later on. Precipitate the lead as sulphide by means of hydrogen sulphide. Let the gas bubble slowly through the cold solution for about half an hour. Let the precipitate settle about an hour. Filter and wash with cold "H_2S water." The precipitate is supposed to be lead sulphide and mercuric sulphide.[1] Incinerate the precipitate in a porcelain crucible at a low temperature [2] in order to burn off the filter-paper. Brush the residue into a 250 c.c. beaker. Wash the crucible with dilute nitric acid and proceed as indicated for lead sulphate (page 326).

The weight of the lead sulphate, multiplied by 0·7360, gives the corresponding amount of lead monoxide—PbO—in the 425 c.c. of solution. Hence, by proportion, calculate the amount in the 500 c.c., that is, in 0·5 grm. of the glaze. The result multiplied by 200 gives the so-called "percentage solubility of the lead frit," or "per cent. of soluble lead" in terms of lead monoxide. The differences obtained in duplicate determinations [3] with quantities of "soluble lead" up to 10 per cent. run to about ±0·1 per cent.; for larger quantities— 20 to 40 per cent. "soluble lead"—differences in the duplicates run about ±0·2 per cent.

§ 162. The Gravimetric Determination of Lead as Molybdate.

Lead can also be advantageously determined as molybdate and as chromate. The advantage of the molybdate precipitation is that the precipitate may be ignited along with the paper, and no particular harm results from a prolonged ignition at a higher temperature than is required to destroy the paper. The errors in manipulation are also reduced more in calculating the weight of the molybdate to PbO than with the corresponding sulphate or chromate. The reaction has been studied in particular by Chatard [4] and Brearley, and Chatard's description of the disturbing effect of an excess of the precipitating agent has led to the process being viewed with a suspicion which the method may not deserve.

Suppose that the lead salt be in solution, add a slight excess of ammonia and then acidify the solution with acetic acid. Add about 5 grms. of ammonium chloride [5] and heat the solution to boiling. An excess of an aqueous solution of ammonium molybdate [6] is then gradually added with constant stirring. Boil

[1] Many glazes contain a little zinc oxide, and some zinc sulphide may be precipitated from the dilute acid with the lead sulphide. Note, other members of the hydrogen sulphide group may be present, and unless a separation is made, the "PbO solubility" will be too high.

[2] If much lead be present, the filter-paper should be ignited alone (page 326). Instead of following the method described in the text, the lead sulphide and filter-paper can be incinerated until the paper is charred to carbon; when nearly cold, carefully add a little fuming nitric acid, a drop at a time, from a pipette, and then a few drops of concentrated sulphuric acid. The carbon will be oxidised, and the lead sulphide transformed into sulphate. Carefully evaporate to dryness, ignite and weigh. This method requires a little practice, but it saves a great deal of time and is more exact than the roundabout method described in the text, once the manipulation is mastered.

[3] It is always advisable to run the "Government Test" in duplicate.

[4] T. M. Chatard, *Chem. News*, **24**, 175, 1871; *Amer. J. Science*, (3), **1**, 416, 1871; J. F. Sacher, *Chem. Ztg.*, **33**, 1257, 1909; H. B. Weiser, *Journ. Phys. Chem.*, **20**, 640, 1916; J. E. Clennell, *Mining Mag.*, **41**, 142, 1929; see page 450.

[5] The precipitate is difficult to filter in the absence of this or some other coagulating salt.

[6] AMMONIUM MOLYBDATE SOLUTION.—Dissolve 34·34 grms. of ammonium heptamolybdate in water; make the solution faintly acid with acetic acid; and make the solution up to a litre (¼E).

the solution two minutes.   Let the cream-coloured precipitate gradually settle until cold.   Filter through a weighed Gooch crucible.   Wash with hot water containing about 2 per cent. of ammonium acetate in solution.   Ignite and weigh as lead molybdate—$PbMoO_4$.   Multiply the weight of the lead molybdate so obtained by 0·6079 to get the corresponding weight of lead monoxide—PbO.

The result is not more than 1 per cent. out with the elements which form water-insoluble molybdates—nickel, zinc, cobalt, manganese, aluminium—and the effects of these elements, together with calcium,[1] strontium and barium, if present, can be eliminated by reprecipitation.   Arsenates and phosphates should not be present.   The slight excess of free molybdic acid which may contaminate the first precipitate is eliminated by reprecipitation.

For reprecipitation, dissolve the precipitate of lead molybdate in hydrochloric acid; heat the solution to boiling; add a sufficient excess of ammonium acetate to neutralise the free hydrochloric acid and proceed as described above.

The lead may be first precipitated as sulphate.   Dissolve the sulphate in a concentrated solution of ammonium acetate and add an excess of ammonium molybdate, as indicated above.   Excellent results can be obtained by this method.

§ 163. Conversion Factors.

In gravimetric analyses it is comparatively rare to find that the constituent to be determined can be weighed directly, as were silica, alumina, ferric oxide and lime.   In most cases the constituent to be determined is separated as an "insoluble" salt, e.g., barium sulphate, lead sulphate, silver chloride, magnesium pyrophosphate, and the corresponding amount of baryta, lead oxide, silver or magnesia determined by multiplying the observed weight by a factor, the so-called conversion factor.   The errors of experiment are obviously multiplied at the same time.   Any error in the preparation and weighing of the precipitate of, say, lead sulphate—$PbSO_4$—in the determination of the lead oxide will be distributed between the lead oxide and the sulphuric anhydride.   In lead sulphate $PbO : SO_3 = 3 : 1$, very nearly; or, more exactly stated, the conversion factor for transforming the lead sulphate to lead oxide is 0·7360.   Hence a total error of $\pm 0\cdot 8$ per cent. in the determination of the lead sulphate corresponds with an error of $\pm 0\cdot 6$ in the determination of the lead oxide.   If the lead be determined as lead molybdate—$PbMoO_4$—we have very nearly $PbO : MoO_3 = 3 : 2$; or, more exactly, the conversion factor for transforming the weight of the lead molybdate to lead oxide is 0·6079.   Hence an error of 0·8 per cent. in the determination of the lead molybdate means that there will be an error of 0·5 in the determination of the lead oxide.   Consequently, other things being equal, *the smaller the factor the less the influence of errors in the determination upon the final result.*   Hence, given two rival analytical processes which are liable to errors of experiment of the same magnitude and which involve the same amount of manipulation, that process will be chosen which has the smaller conversion factor.   For this reason, among others, silver is better precipitated as bromide than as chloride.   The conversion factor in the former case is 0·5744, and in the latter 0·7525.   As a matter of fact, in spite of the theoretical advantages of the bromide process, the chloride process is preferred by many because the sources of error and corrections have been well explored for the chloride process but not for the bromide process.

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[1] Calcium molybdate is very prone to precipitation with the lead molybdate.

§ 164. The Volumetric Determination of Lead—
Molybdate Process.

Schindler, in 1888, proposed to determine lead as lead molybdate by means of a standard solution of ammonium molybdate. The titration is made in a hot ammonium acetate solution of lead sulphate slightly acidified with acetic acid.[1] The reaction is symbolised:

$$Pb(C_2H_3O_2)_2 + (NH_4)_2MoO_4 \rightarrow PbMoO_4 + 2NH_4C_2H_3O_2$$

According to Kroupa, the presence of arsenic, antimony, bismuth, phosphorus and zinc does not interfere with the process. Barium and strontium salts lead to low results. These substances appear to act by retarding the dissolution of the lead sulphate. The difficulty is overcome by repeatedly boiling the sulphate with hot ammonium acetate to ensure complete solution.[2] Bannister and McNamara found that the results are high if calcium salts be present. E.g., with test solutions containing the equivalent of 0·2005 grm. of lead and 0 to 0·2415 grm. of calcium sulphate, the results ranged from 100 to 109 per cent. of lead in place of 100.

1 gram of the lead compound—say, white lead—is dissolved in acetic or 5 per cent. nitric acid; for the dissolution of red lead, see page 331. Any insoluble sulphates are filtered off and the residue well washed. 10 per cent. sulphuric acid is added to the filtrate, drop by drop, until there is no further precipitation of lead sulphate. The precipitated sulphates are filtered off and well washed with approximately 1·0N-sulphuric acid in order to remove any calcium sulphate, otherwise the results will be high. Puncture the apex of the filter-paper and dissolve the precipitate off the paper in the *minimum* [3] quantity of a hot concentrated solution of ammonium acetate.[4] Make the solution up to 250 c.c. in a graduated flask and shake well. Acidify 50 c.c. of the solution with 2–3 c.c. of acetic acid, and heat to boiling. Titrate the hot solution with standard ammonium molybdate [5] from a burette until a drop gives a slight but

[1] C. Schindler, *Zeit. anal. Chem.*, 27, 137, 1888; H. Weber, *ib.*, 42, 628, 1903; I. C. Bull, *ib.*, 41, 653, 1902; *School Min. Quart.*, 23, 348, 1903; *Chem. News*, 87, 40, 52, 66, 1903; H. H. Alexander, *Eng. Min. Journ.*, 55, 298, 1893; *Chem. Centr.*, ii, 293, 1893; J. A. Müller, *Bull. Soc. chim.*, (3), 31, 1303, 1904; R. Kroupa, *Berg. Hütt. Ztg.*, 53, 411, 1894; J. F. Sacher, *Chem. Ztg.*, 33, 1257, 1900; C. O. Bannister and W. McNamara, *Analyst*, 37, 242, 1912; L. M. Iolson and E. M. Tall, *Zeit. anal. Chem.*, 108, 96, 1937. See *Chem. Eng.*, 16, 36, 1912; R. C. Wiley, P. M. Ambrose and A. D. Bowers, *Ind. Eng. Chem. Anal. Ed.*, 2, 415, 1930; H. E. French, *Canadian Mining Journ.*, 53, 504, 1932. For the precipitation of lead as chromate, followed by treatment with potassium iodide and sulphuric acid and subsequent titration of the liberated iodine with thiosulphate, see A. Longi and L. Bonavia. *Gazz. Chim. Ital.*, 26, i, 327, 1896; *Zeit. anorg. Chem.*, 17, 158, 1898; J. Waddell, *Analyst*, 41, 270, 1916; C. W. Simmons, J. R. Gordon and H. C. Boehmer, *Canad. Chem. Journ.*, 4, 139, 1920; I. M. Kolthoff, *Pharm. Weekblad*, 57, 934, 1920; W. W. Scott, *Ind. Eng. Chem.*, 17, 678, 1925; H. Eisenlohr, *Sprech.*, 43, 389, 1910; G. Cervi, *Chem. Zentr.*, ii, 1343, 1904; B. Oddo and A. Beretta, *Gazz. Chim. Ital.*, 39, i, 671, 1909.

[2] Compare J. Majdel, *Zeit. anal. Chem.*, 83, 36, 1931; W. W. Scott and S. M. Alldredge, *Ind. Eng. Chem. Anal. Ed.*, 3, 32, 1931.

[3] High results will be obtained if excess ammonium acetate be used—V. Lindt, *Zeit. anal. Chem.*, 57, 71, 1918.

[4] AMMONIUM ACETATE SOLUTION.—Add 50 per cent. acetic acid to ammonia solution (sp. gr. 0·91) until the mixture is just acid to litmus—Lindt, *loc. cit.*

[5] STANDARD AMMONIUM MOLYBDATE SOLUTION.—Dissolve 7·913 grms. of ammonium molybdate (see footnote 1, page 673) in water and dilute the solution to a litre. If the solution be turbid, add some ammonia before the dilution is completed—1 c.c. will be nearly equivalent to 0·01 grm. PbO. To standardise the solution, dissolve, say, five known amounts of freshly precipitated lead sulphate in hot ammonium acetate; add 2–3 c.c. of acetic acid and titrate as indicated in the text. See also J. E. Clennell, *Mining Mag.*, 57, 28, 1937. Schindler also uses the converse reaction, titration with standard lead acetate, for the volumetric determination of molybdenum.

distinct yellow coloration when added to a drop of freshly prepared [1] aqueous solution of tannin on a glazed tile—spot test. If the solution cools appreciably during the titration, it should be heated again to finish the titration.

If tungsten be present in the form of tungstic acid—WO_3—the latter may react with the lead acetate, produced by double decomposition between the lead sulphate and ammonium acetate, to give lead tungstate—

$$Pb(C_2H_3O_2)_2 + (NH_4)_2WO_4 = PbWO_4 + 2NH_4C_2H_3O_2$$

If enough tungsten be present to combine with all the lead, a negative result will be obtained. Hence tungsten must be removed before the lead is determined.[2]

Titrating with "Spot-test" Indicators.—It is easy to over-titrate the solution when using "spot-test" indicators and three methods of titrating to rectify or avoid over-titration may be indicated: (1) Some prefer to use a standard solution of lead nitrate [3] for checking the first titration. Suppose the titration is finished, add 10 c.c. of a standard lead nitrate solution and continue the titration. 0·1 grm. of lead oxide must be subtracted from the result of the titration.

(2) For the titration place half the solution to be titrated in a separate beaker and titrate the other half by adding a cubic centimetre of the ammonium molybdate solution at a time, in order to get a rough idea of the amount needed. Suppose the one portion requires between 15 and 16 c.c. for the titration (no coloration with 15 c.c.; yellowish-brown coloration with 16 c.c.). Add the untitrated portion to the portion just titrated; 14 c.c. can now be safely run from the burette and the titration finished by small additions from the burette.

(3) In titrating with a spot test, particularly with slow reactions, the testing should be done systematically. Suppose the first stop be made at 29 c.c., the second at 29·2 c.c., the third at 29·4 c.c., and so on. If the brown coloration develops on the sixth stop, it would mean that $29 + (n - 1)0·2 = 30·0$ c.c. has been added $(n = 6)$. But the coloration may subsequently develop on the fourth stop *after* it has been passed. It is then easy to determine the burette reading for the fourth stop—namely, $29 + (n - 1)0·2 = 29·6$ c.c., where $n = 4$.

Lead carbonate may also be precipitated by the addition of ammonium carbonate, the precipitate dissolved in acetic acid, and the solution titrated

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[1] TANNIN SOLUTION.—About 0·5 grm. of tannin dissolved in 100 c.c. of water. Ammonium molybdate gives with tannin a coloration varying from blood-red to a pale yellow, according to the concentration of the solutions. The colour is visible with a dilution 1 : 400,000 (Schindler). Lead molybdate gives no coloration. Concentrated solutions of lead acetate give a faint greenish-yellow colour, which cannot be confused with the coloration due to ammonium molybdate. J. L. Danziger uses a solution formed by saturating acetic acid with crystalline stannic chloride and saturating the solution with ammonium thiocyanate. When this is used instead of tannin as indicator, the end of the reaction is indicated by a pink coloration—spot test. J. F. Sacher (*Koll. Zeit.*, 19, 276, 1916) uses no indicator, but determines the end-point by the sudden disappearance of the turbidity of the solution when the reaction is just complete. The turbidity is due to colloidal lead molybdate. For the use of Alizarine red as an internal adsorption indicator, see T. Raïkhinshteïn and N. Korobov, *Journ. Gen. Chem. (U.S.S.R.)*, 2, 661, 1932; *ib.*, 3, 531, 1933. E. J. Kocsis and L. Pollak (*Acta Lit. Sci. Univ. Hung. Fran. Joseph Sect. Chem. Min. Phys.*, 4, 147, 1934) advocate the use of Congo red or Tropæoline 00 as internal indicators; and C. Candea and I. G. Murgulescu (*Ann. Chim. anal. Chim. appl.*, 18, 33, 1936) 20 drops of a 0·5 per cent. solution of Eosin A.

[2] H. Lavers, *Min. Eng. World*, 40, 54, 1914.

[3] LEAD NITRATE SOLUTION.—14·84 grms. of lead nitrate per litre corresponds with 0·01 grm. lead oxide per c.c.

with potassium ferrocyanide,[1] as indicated under zinc. The results are good.[2]

§ 165. The Electrolytic Process for the Determination of Lead.

Metallic lead can be readily deposited from alkaline electrolytes containing, e.g., phosphates, alkali plumbate, double oxalates, double cyanides.[3] But it is so difficult to dry the lead for weighing without oxidation, that it is considered better to take advantage of the fact that lead is deposited from acid solutions in the form of lead dioxide—PbO_2—on the anode, not the cathode.[4] Hence the dish, with its inner surface matt, is fitted as described on page 254, fig. 80; but the direction of the current is reversed so that the dish is the anode, and the platinum disc the cathode. The details indicated on page 255 are to be followed with the modifications indicated in the following paragraphs.

The Electrolyte.—Suppose that 1 grm. of lead nitrate be dissolved in 30 c.c. of distilled water. Add 25–35 c.c. of concentrated nitric acid. Dilute the solution to 150–160 c.c.

The Electrolysis.—Electrolyse the solution with a current density of 0·5 to 1·8 amps.,[5] and a voltage of 2·0 to 2·5 volts, at atmospheric temperature.[6] As soon as the electrical circuit is closed a yellow deposit appears on the anode (dish), which becomes orange, red and finally dark brown or black. The electrolysis occupies between 2 and 3 hours.[7] If a deposit of metallic lead

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[1] M. Yvon, *Journ. Pharm. Chem.*, (5), 19, 18, 1889; A. H. Low, *Journ. Amer. Chem. Soc.*, 15, 548, 1893; E. Müller, *Zeit. angew. Chem.*, 32, 351, 1919; W. D. Treadwell and D. Chervet, *Helv. Chim. Acta*, 5, 633, 1919; E. Müller and K. Gäbler, *Zeit. anal. Chem.*, 62, 29, 1923; R. Burstein, *Zeit. anorg. Chem.*, 164, 219, 1927.

[2] For the determination of lead in nearly neutral solution by titration with standard potassium sulphate using fluorescein as external indicator, see S. N. Roy, *Journ. Indian Chem. Soc.*, 12, 584, 1935.

[3] G. Parodi and A. Mascazzini, *Gazz. Chim. Ital.*, 7, 222, 1877; A. Riche, *Ann. Chim. Phys.*, (5), 13, 508, 1878; C. Luckow, *Zeit. anal. Chem.*, 19, 1, 1880; H. S. Warwick, *Zeit. anorg. Chem.*, 1, 285, 1893; A. F. Linn, *Journ. Amer. Chem. Soc.*, 24, 435, 1902; K. Elbs and F. W. Rixon, *Elektrochem. Zeit.*, 9, 267, 1903. R. Gartenmeister (*Chem. Ztg.*, 37, 1281, 1913) uses gallic acid for preventing the deposition of lead dioxide on the anode and the evolution of hydrogen on the cathode.

[4] A. Riche, *Ann. Chim. Phys.*, (5), 13, 508, 1878; C. Luckow, *Zeit. anal. Chem.*, 19, 1, 1880; L. Schucht, *ib.*, 22, 485, 1883; F. Tenney, *Amer. Chem. Journ.*, 5, 413, 1884; L. Medicus, *Ber.*, 25, 2490, 1892; A. Classen, *ib.*, 21, 359, 1888; 27, 163, 1894; H. Biltz, *ib.*, 58B, 913, 1925; A. Kreichgauer, *ib.*, 27, 315, 1894; *Zeit. anorg. Chem.*, 9, 89, 1895; *Zur quantitativen Bestimmung des Bleis*, Würzburg, 1894; F. Rüdorff, *Zeit. angew. Chem.*, 5, 3, 197, 1892; E. F. Smith and J. C. Saltar, *Zeit. anorg. Chem.*, 3, 415, 1893; F. A. Gooch and F. B. Beyer, *ib.*, 61, 286, 1909; *Amer. Journ. Sci.*, (4), 27, 59, 1909; G. Meillère, *Journ. Pharm. Chim.*, (6), 16, 465, 1902; H. Danneel and H. Nissenson, *Inter. Cong. angew. Chem.*, 4, 677, 1903; A. Fischer and R. J. Boddaert, *Elektrochem. Zeit.*, 10, 945, 1904; H. J. S. Sand, *Journ. Chem. Soc.*, 91, 397, 1907; *Trans. Faraday Soc.*, 5, 207, 1910; F. S. Kipping *et al.*, *Brit. Assoc. Rep.*, 79, 1910; L. Bertiaux, *Ann. Chim. anal.*, 18, 217, 1913; I. Compagno, *Ann. Chim. appl.*, 3, 164, 1915; J. Milbauer and I. Setlik, *Journ. prakt. Chem.*, (2), 99, ii, 85, 1919; A. V. Pamfilov and A. A. Blagonravova, *Journ. Russ. Phys. Chem. Soc.*, 60, 699, 1928; W. T. Schrenk and P. H. Delano, *Ind. Eng. Chem. Anal. Ed.*, 3, 27, 1931; B. Jones, *Analyst*, 58, 11, 1933; M. Bertiaux, *Documentation Sci.*, 2, 72, 1933.

[5] For an overnight electrolysis (10–12 hours) use a current density of 0·5 amp.

[6] If the operation be conducted at 50°–55°, the time required for the electrolysis is shortened to between 1 and 1½ hours, using a current density of 1·3 to 1·6 amps., and 2·2 to 2·6 volts. According to J. G. Fairchild (*Journ. Ind. Eng. Chem.*, 3, 902, 1911), the essential conditions for good deposits are: (1) hot solutions (50°–60°); and (2) an initial low amperage.

[7] To recognise the end of the electrolysis, withdraw a few drops of the solution from the dish; make the solution alkaline with ammonia; add a few drops of H_2S water, or ammonium sulphide, when a black or dark brown precipitate of lead sulphide shows that the electrolysis is not completed; other recognised qualitative tests for lead can be used. If the level of the electrolyte be raised a little by the addition of distilled water, the appearance of a yellow or orange film on the newly immersed surface of the anode also shows that the electrolysis is not ended.

should appear on the platinum disc (cathode) during the electrolysis, add a little more concentrated nitric acid or interrupt the current for about half a minute during the middle and towards the end of the electrolysis.

When the electrolysis is complete, the deposit is washed with water, absolute alcohol and absolute ether in the usual way. If the electrolyte be syphoned off before the current is stopped (fig. 83, page 257), keep the deposit quite covered with liquid all the time the syphon is in action. In other words, pour distilled water into the dish as fast as acid is syphoned off.

Drying and Weighing the Lead Dioxide.—The lead dioxide retains water with great tenacity,[1] and the results will be too high if the regular factor—0·8662—for converting the lead dioxide into the equivalent amount of metallic lead be employed. Classen recommended drying the lead dioxide at 180–190°, and Hollard at 200°. Smith has shown that deposits of lead dioxide approximately 0·5 grm. in weight do not really have a constant composition until they have been dried at 230°. For instance, with a deposit containing the equivalent of 0·4992 grm. of lead:—

Time heated . .	30	30	30	30	30	min.
Temperature . .	200°	200°	230°	240°	270°	
PbO_2 . . .	0·5788	0·5790	0·5780	0·5780	0·5780	grm.

Similarly, with the equivalent of approximately 0·25 grm. of lead, the lead dioxide attains a constant weight at 200°. In the former case, the factor of conversion corresponds with the empirical value 0·8637; and in the latter case, 0·8643. With smaller quantities of the dioxide, say, 0·05 to 0·1 grm., a special factor is not needed. Fischer recommends the following empirical factors:—

Amount of Pb .	Below 0·1	0·1	0·1 to 0·3	0·5	1·0 grm.
Factor . .	0·8660	0·8658	0·8652	0·8629	0·8610

Instead of following this procedure, May[2] recommends gentle ignition of the dioxide at a low temperature to convert the dioxide into lead monoxide—PbO—before weighing. The results are then excellent. Thus, Treadwell gives for four experiments:

					Mean.
PbO_2 found. .	0·2202	0·2200	0·2203	0·2202	0·2202 grm.
PbO found . .	0·2042	0·2046	0·2043	0·2044	0·2044 grm.

In another series of trials the following average results were obtained:

Lead used in each trial	0·1898 grm.
Lead found by weighing as PbO_2	0·1907 grm.
Lead found by converting $PbO_2 \rightarrow PbO$ . . .	0·1898 grm.

Removing the Deposited Lead Peroxide from the Electrode.—Digest the dioxide with nitric acid to which a little hydrogen peroxide has been added (say, 1 c.c.). The lead dissolves easily and quickly. Smith recommends removing the deposit by the action of dilute nitric acid along with a rod of copper or zinc.

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[1] It is very doubtful if the excessive weight of the lead dioxide is due to the formation of a higher oxide. A. Hollard, *Bull. Soc. chim.*, (3), **29**, 151, 1903; (3), **31**, 239, 1904; *Compt. rend.*, **136**, 229, 1904; *Chem. News*, **79**, 122, 1899; R. O. Smith, *Journ. Amer. Chem. Soc.*, **27**, 1287, 1905; R. C. Benner, *Journ. Ind. Eng. Chem.*, **2**, 348, 1910; J. G. Fairchild, *ib.*, **3**, 902, 1911; F. Utz, *Chem. Zentr.*, ii, 1788, 1912.

[2] W. C. May, *Amer. J. Science*, (3), **6**, 255, 1873; F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, **2**, 148, 1911; H. J. S. Sand, *Chem. News*, **100**, 269, 1909; A. V. Pamfilov and A. A. Blagonravona, *Journ. Russ. Phys. Chem. Soc.*, **60**, 699, 1928.

Henz [1] recommends a solution of sodium or potassium nitrite acidified with nitric acid.

Preparation of Lead Sulphate for Electrolysis.—Lead is commonly separated as sulphate in gravimetric work. According to Classen, lead sulphate is brought into a condition for electrolysis by warming the precipitated lead sulphate with an excess of ammonia, whereby lead hydroxide is formed. Pour the mixture with constant stirring into a platinum dish containing about 20 c.c. of warm concentrated nitric acid. If any lead sulphate appears as a precipitate, it will soon dissolve in the solution. The solution is then ready for electrolysis.

Lead sulphate is also brought into a condition for electrolysis by dissolving it in ammonium acetate, adding 20 c.c. of concentrated nitric acid and electrolysing the solution at 60° with a current density of 1·5 to 1·7 amps.[2]

Marie [3] places the lead sulphate in the dish to be used for the electrolysis; the dish is heated on the water bath along with some dilute nitric acid. Gradually add crystals of ammonium nitrate until all is dissolved. Every 0·3 grm. of lead sulphate requires 5 grms. of ammonium nitrate. Dilute the solution with warm water so that the liquid contains about 10 per cent. of free acid and electrolyse the solution at 60°–70°. For lead silicate, decompose the fine powder with sulphuric and hydrofluoric acids. Too great an excess of sulphuric acid prevents the solution of lead sulphate by the ammonium nitrate.[4]

Effect of Foreign Electrolytes.—The process indicated above will separate lead from the alkalies, alkaline earths, chromium, beryllium, zirconium, iron, uranium, zinc, nickel, cobalt and cadmium. Chlorides should be absent from the electrolyte.[5] The determination of lead by this process in the presence of appreciable amounts of arsenic will be unreliable.[6] The results will be low. Classen says that "when enough (0·5 grm.) is present, no lead will be deposited as dioxide on the anode, but metallic lead mixed with arsenic will be deposited on the cathode. If the electrolysis be continued for some time, the arsenic will be gradually driven from the cathode as arsenic hydride, and the precipitated lead will pass into solution. Finally, if the electrolysis be sufficiently prolonged, all the lead will be deposited as dioxide on the anode." The action of selenium is similar. According to Vortmann [7] the results are high in the presence of sulphuric, selenic and chromic acids. Hence he recommends reprecipitation by electrolysis. In the presence of arsenic and phosphorus the results will be low. In that case Vortmann recommends depositing the metal as lead on the cathode, dissolving the metal in nitric acid and reprecipitating the lead as dioxide.

§ 166. The Rapid Deposition of Lead Dioxide by a Rotating Electrode—Exner's Process.

The enormous gain in the speed of deposition which attends the use of a rotating electrode removes one of the most serious objections to electro-analysis.

[1] F. Henz, *Zeit. anorg. Chem.*, **37**, 2, 1903.

[2] H. Nissenson and B. Neumann, *Chem. Ztg.*, **19**, 1142, 1895.

[3] C. Marie, *Compt. rend.*, **130**, 1032, 1900; *Chem. News*, **82**, 51, 1900.

[4] For lead chromate, Marie proceeds in a similar manner, but less ammonium nitrate is needed—2 grms. of ammonium nitrate suffice for 0·5 grm. of lead chromate.

[5] When chlorides are present, evaporation with sulphuric acid and treatment of the sulphate as described in the text will furnish a solution ready for electrolysis. W. T. Schrenk and P. H. Delano (*Ind. Eng. Chem. Anal. Ed.*, **3**, 27, 1931) find that silver, bismuth, manganese, tin, arsenic, antimony, mercury, chromates and phosphates, in more than very small quantities, inhibit deposition or may be deposited with the lead dioxide or cause scaling.

[6] B. Neumann, *Chem. Ztg.*, **20**, 382, 1896.

[7] G. Vortmann, *Liebig's Ann.*, **351**, 283, 1907. For the effect of gums and colloids generally, see H. Freundlich and J. Fischer, *Elektrochem. Zeit.*, **18**, 885, 1912.

In the case of copper, for example, a rotating anode enables a satisfactory determination to be made in 5 minutes, using a current of 10 volts and 13 amps., nickel in 15 minutes, cobalt in half an hour and cadmium in 5 minutes. The following diagram (fig. 92), after Fischer, emphasises very forcibly the great
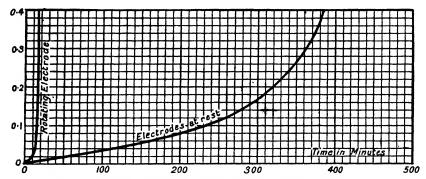

FIG. 92.—Time of Deposition, Stationary and Rotating Electrodes.

gain in time obtained by the use of rotating electrodes. The ordinates show the amounts of copper precipitated by rotating and stationary electrodes after the elapse of different intervals of time (abscissæ).

Knobukow [1] introduced rotating electrodes in electro-analysis in 1886, but the subject did not attract much attention until the American chemists— Gooch and Smith—took up the subject about 1903. These chemists and their co-workers extended Knobukow's idea, and showed that a still further gain in time attends the use of currents of greater density and voltage. For further details see the works cited on page 253.

The Apparatus.—The determination of lead as dioxide by the use of rotating electrodes may now be described, on the assumption that pages 250 to 259 have been digested. Fit up the apparatus illustrated in fig. 93 -- the lettering is similar to that in figs. 79 and 80, the difference being that the platinum dish is here used as the anode, not the cathode. The current accordingly passes through the electrolytic cell in the reverse direction to what was the case with copper. The disc electrode is replaced by a flat spiral of heavy platinum wire with the spirals fixed in position by twisted platinum binding wires.[2] The centre of the spiral is depressed to give it the form of a shallow bowl about 5 cm. in diameter. The stem of the electrode is clamped to the axis of a wheel which can be rotated by a motor or turbine at between 450 and 600 revolutions per minute and yet be in electrical contact with the battery.

The Electrolysis.—The solution, prepared as indicated in the preceding section for stationary electrodes, is placed in a platinum basin, matted on its inner surface. Add 20 c.c. of concentrated nitric acid and dilute the solution to make a total volume of 110–125 c.c. Heat the solution to about 70° and

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[1] N. von Knobukow, *Journ. prakt. Chem.*, (2), **33**, 473, 1886; F. A. Gooch and H. E. Medway, *Amer. J. Science*, (4), **15**, 320, 1903; F. F. Exner, *Journ. Amer. Chem. Soc.*, **25**, 896, 1903; R. O. Smith, *ib.*, **27**, 1287, 1905; E. F. Smith, *Electro-Analysis*, Philadelphia, 40, 1918; F. M. Perkin, *Elektrochem. Zeit.*, **10**, 477, 1904.

[2] See E. F. Smith, *loc. cit.*, 43. Numerous types of cells for rotating electrodes have been devised—some are described in the text-books indicated on page 253. That described in the text may be the simplest but not necessarily the best when many determinations have to be made.

start the electrode rotating at about 500 revolutions per minute.[1] A current of electricity at 4–5 volts, and current density 10–11 amps., is passed through the solution. The lead will soon be deposited as a black adherent velvety film of dioxide on the dish. The maximum period required for 0·25 grm. of the metal was found by Smith to be 15 minutes, and for 0·5 grm., 25 minutes.[2]
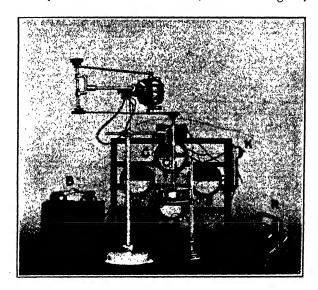
Fig. 93.—Electrolysis by Rotating Electrode.

Smith found that the rate of precipitation from a solution containing the equivalent of 0·5787 grm. of lead dioxide was as follows:—

Time			5	10	15	20	25	30	min.
PbO_2	.	.	0·4940	0·5708	0·5747	0·5770	0·5787	0·5789	grm.

In about 25 minutes, when the decomposition is finished, stop the rotator and reduce the current by the introduction of resistance. Add water to cover the lead peroxide; syphon off the acid while keeping the dish full of water. Wash the deposit with alcohol and ether in the usual way.[3]

To illustrate the results which might be expected:

PbO_2 found		.	0·0566	0·1137	0·2887	0·5781	0·5788	grm.
Pb (by factor 0·8662)	.	0·0490	0·0985	0·2501	0·5008	0·5015	grm.
Pb (used)	.	.	0·0491	0·0982	0·2496	0·4992	0·4996	grm.

The calculation of the amount of lead corresponding with the deposited lead dioxide here presents the same difficulty as was encountered in dealing with stationary electrodes. The factor 0·8662 gives too high results.

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[1] There is no need to heat the solution during the electrolysis, because the high current used keeps the liquid hot. With higher speeds the electrolyte may sweep round the edge of the dish and be thrown against the cover glass. This will do no particular harm if the amount of liquid in the basin does not exceed 125 c.c.

[2] F. F. Exner, *Journ. Amer. Chem. Soc.*, **25**, 896, 1903; R. O. Smith, *ib.*, **27**, 1287, 1905.

[3] For the simultaneous determination of copper and lead with rotating anodes, see A. J. White, *Trans. Amer. Electrochem. Soc.*, **24**, 297, 1913; W. Gemmell, *Journ. Soc. Chem. Ind.*, **32**, 581, 1913; H. Biltz, *Ber.*, **58B**, 913, 1925.

§ 167. The Colorimetric Determination of Lead.

Pelouze [1] first proposed to determine small amounts of lead in a given solution from the intensity of the brown coloration [2] produced when the lead is converted into sulphide.[3] The method has been frequently used for determining the small amounts of lead in water, citric acid and other substances.[4] The method has also been recommended for the determination of the amount of lead in factory dusts and glazes.[5] The results are usually too low in presence of traces of free acid—acetic or hydrochloric acid—since some lead is not then converted into the sulphide. This will be obvious from our study of the action of hydrogen sulphide on lead salts in acid solutions (page 272). The results are very much better in alkaline solutions using sodium or ammonium sulphide as precipitant.

[1] T. J. Pelouze, *Ann. Chim. Phys.*, (3), **79**, 108, 1841.

[2] It is possible to detect 1 part of lead per 16,000 parts of solution, according to F. Jackson (*Journ. Amer. Chem. Soc.*, **25**, 992, 1903); 1 : 26,900, according to T. G. Wormley (*Chem. News*, **16**, 302, 1867; *Micro-Chemistry of Poisons*, New York, 1867); and 1 : 1,000,000, according to A. B. Prescott and E. C. Sullivan, and R. Warington (*Journ. Soc. Chem. Ind.*, **12**, 97, 1893); C. H. Pfaff, *Handbuch der analytischen Chemie*, Altona, **1**, 68, 150, 161, 1821; J. L. Lassaigne, *Journ. Chim. Méd.*, **8**, 581, 1832; P. Harting, *Journ. prakt. Chem.*, (1), **22**, 45, 1841; E. Eegriwe, *Festschrift Riga Polyt. Inst.*, 103, 1912; *Zeit. anal. Chem.*, **53**, 420, 1914; R. Wildenstein, *ib.*, **2**, 9, 1863; J. S. C. Wells, *Analyst*, **12**, 173, 1887; B. Neumann, *Chem. Ztg.*, **20**, 763, 1896.

[3] A. Trillat (*Compt. rend.*, **136**, 1205, 1903), A. D. Petrov (*Journ. Russ. Phys. Chem. Soc.*, **60**, 311, 1928), A. Seisner, A. Necke and H. Müller (*Zeit. angew. Chem.*, **42**, 96, 1929) showed that lead peroxide produces a blue coloration in contact with tetramethyldiaminodiphenyl-methane in a solution acidified with acetic acid. By converting the lead into peroxide the amount of lead is determined from the intensity of the blue coloration; the results are far from satisfactory. Similar attempts to convert the lead into peroxide and subsequently bringing the peroxide in contact with a solution of potassium iodide and determining the amount of lead from the intensity of the colour of the liberated iodine—in the presence and in the absence of starch—likewise failed to give constant results without an abnormal expenditure of time in isolating the lead peroxide. The chromate precipitation has also been recommended as a turbidimetric process (C. G. Egeling, *Pharm. Weekblad*, **44**, 338, 1907) but is unreliable—K. Scheringa, *ib.*, **47**, 1212, 1910; P. A. Meerburg, *Chem. Weekblad*, **10**, 752, 1913.

[4] J. M. Wilkie, *Journ. Soc. Chem. Ind.*, **28**, 636, 1909; R. Warington, *ib.*, **12**, 97, 1893; C. A. Hill, *Chemist Druggist*, **66**, 388, 1905; H. W. Woudstra, *Zeit. anorg. Chem.*, **58**, 168, 1908; F. L. Teed, *Analyst*, **17**, 142, 1892; E. R. Budden and H. Hardy, *ib.*, **19**, 169, 1894; B. Kühn, *Arbeit. Kais. Gesund.*, **23**, 389, 1906; A. G. V. Harcourt, *Journ. Chem. Soc.*, **97**, 841, 1910; M. Lucas, *Bull. Soc. chim.*, (3), **15**, 39, 1896; A. Liebrich, *Chem. Ztg.*, **22**, 225, 1898; G. Bischof, *Zeit. anal. Chem.*, **18**, 73, 1879; V. Antony and T. Benelli, *Gazz. Chim. Ital.*, **1**, 218, 1871; **2**, 194, 1872; P. Carles, *Journ. Pharm. Chim.*, (6), **12**, 517, 1900; L. Liebermann, *Pharm. Centralhalle*, **29**, 10, 1889; M. M. P. Muir, *Chem. News*, **33**, 11, 1876; R. Meldrum, *ib.*, **117**, 49, 1918; C. Reese and J. Drost, *Zeit. angew. Chem.*, **27**, 307, 1914; I. M. Siegfried and W. Pozzi, *Biochem. Zeit.*, **61**, 149, 1914; H. Pick, *Chem. Zentr.*, ii, 1366, 1914; *Arbeit. Kais. Gesund.*, **48**, 155, 1914; K. Beck, Löwe and P. Stegmuller, *ib.*, **33**, ii, 203, 1910; Fauconnier, *Ann. Chim. anal.*, **20**, 126, 1915; D. Avery, A. J. Hemingway, V. G. Anderson and T. A. Read, *Proc. Austral. Inst. Min. Met.*, 173, 1921; J. C. Thresh, *Analyst*, **46**, 270, 1921; **49**, 124, 1924; J. H. Hamence, *ib.*, **57**, 622, 1932; **58**, 461, 1933; **59**, 274, 1934; A. G. Francis, C. O. Harvey and J. L. Buchan, *ib.*, **54**, 725, 1929; N. L. Allport and G. H. Skrimshire, *ib.*, **57**, 440, 1932; *Pharm. Journ.*, **129**, 248, 1932; C. Pyriki, *Zeit. anal. Chem.*, **64**, 325, 1924; A. L. Bernoulli, *Helv. Chim. Acta*, **9**, 827, 1926; O. Liebknecht and L. Gerb, *Angew. Chem.*, **45**, 744, 1932; H. D. Thornton, *Journ. Inst. Chem.*, 115, 1933; M. Randall and M. N. Sarquis, *Ind. Eng. Chem. Anal. Ed.*, **7**, 2, 1935; H. J. Wickmann and F. A. Vorkes, *Journ. Assoc. Off. Agr. Chem.*, **17**, 119, 1934; A. Mâcheboeuf, H. Cheftel and J. Blass, *Compt. rend.*, **195**, 146, 1932; J. C. Thresh, J. F. Beale and E. V. Suckling, *The Examination of Water and Water Supplies*, London, 1933; P. G. Jackson, *Journ. Soc. Chem. Ind.*, **56**, 211T, 1937. L. W. Winkler (*Zeit. angew. Chem.*, **26**, 38, 1913) recommends addition of ammonium chloride to get more reliable results.

[5] H. R. Rogers, *Report Departmental Committee appointed to inquire into the Dangers incident on the Use of Lead*, **2**, 118, 1910; A. G. V. Harcourt, *ib.*, **2**, 120, 1910; A. Gronover and E. Wohnlich, *Zeit. Untersuch. Lebensm.*, **63**, 623, 1932. Rogers's method cannot be regarded seriously as a quantitative process.

Influence of Iron Salts.—Dark brown iron sulphide is precipitated in alkaline solutions and, since traces of iron are nearly always associated with lead, it is necessary to eliminate the disturbing effects produced by this agent. Warington used the colorimetric process for determining small quantities of lead in citric and tartaric acids and, in order to avoid the effects produced by iron, he recommends making the solution "alkaline with ammonia, treating the solution with a few drops of potassium cyanide, and heating it to near the boiling point." The iron is thus converted into a complex cyanide—probably ferrocyanide—and it is not then affected by the subsequent addition of alkali sulphide. The method works quite satisfactorily provided the iron is all present in the ferrous condition and the liquid is strongly alkaline. Ferric salts are not converted by the treatment with potassium cyanide into colourless substances unaffected by alkali sulphides. It is therefore necessary to reduce ferric salts to the ferrous condition before applying the test. Wilkie recommends sodium thiosulphate in acid solution as a reducing agent. Its action is probably represented by the equation:—

$$2Na_2S_2O_3 + 2FeCl_3 = 2FeCl_2 + Na_2S_4O_6 + 2NaCl$$

On the other hand, in spite of the influence of free acid on the intensity of coloration, several authorities recommend that the determination be carried out in faintly acid solution to eliminate the effect of iron salts.

The Determination.—Wilkie made an artificial mixture of 12 grms. of citric acid, 0·004 grm. of ferric iron and 0·00005 grm. of lead. This mixture was placed in a "Jena flask and made up to about 35 c.c. with water. 2 c.c. of 0·1N-sodium thiosulphate [1] were then added, and the whole heated to incipient boiling, and the flame removed. After about 5 minutes the solution became perfectly water-white, and to it was immediately added 1 c.c. of a 10 per cent. solution of potassium cyanide,[2] and then [3] an excess (13 c.c.) of 0·880 ammonia, and the whole gently boiled until colourless."

Assuming that the solution under investigation is treated as the mixture just described, a similar solution is made with a known amount of lead. This solution is systematically diluted with water in Nessler's glasses, and one drop of ammonium sulphide [4] added to each. The colours so obtained are compared with that of the solution under investigation in the usual way—see Colorimetry.[5]

Disturbing Factors.—Woudstra found that with the colorimetric process:

Lead present	.	0·001	0·0009 grm.
Estimated lead in error	− 18 to − 8	+ 11·1 to − 3·3 per cent.	

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[1] It is very necessary to test all the reagents used to ensure their freedom from traces of lead.

[2] It is best to use an excess of potassium cyanide, say 25 of potassium cyanide to 1 of iron.

[3] Wilkie considers that the results are better if the potassium cyanide is added to the acid solution before the ammonia, since the formation of the ferrocyanide proceeds faster in the acid solution.

[4] According to Warington, ammonium sulphide is a more delicate reagent than hydrogen sulphide.

[5] A. G. V. Harcourt (*Journ. Chem. Soc.*, 97, 841, 1910) makes a series of permanent colour standards matching the tints of solutions containing different amounts of lead. The colour standards are made from mixtures of ferric, cobalt and copper sulphates in suitable proportions. These are labelled and preserved in hermetically sealed glass cylinders. J. W. Lovibond (*Measurement of Light and Colour Sensations*, London, 124, 1910) made combinations of his standard glass slips to match the tints of solutions containing known amounts of lead.

It must be borne in mind that the lead sulphide precipitated in alkaline solution is colloidal,[1] and that the tint is to some extent determined by the size of the colloidal particles, which, in turn, is dependent upon the nature of the salts in the solution under investigation and on slight variations in the way the solution has been prepared. Vigorous agitation, for instance, may coagulate the suspended colloid and cause a precipitation of the lead sulphide. Salts of the alkalies and alkaline earths rapidly coagulate the colloidal sulphide. According to Kühn, barium chloride is 100 times more active than sodium nitrate in coagulating the suspended colloid.

Sometimes the colloidal sulphide imparts a smoky opalescence to the solution. This is not favourable for satisfactory comparisons. Warington recommended the addition of (approximately) an equal volume of glycerol to the solution under investigation; Siegfried and Pozzi, one-hundredth part by volume of a 1 per cent. solution of the purest gum arabic; and Harcourt, mixing the solution with about one-fifth its volume of a clear solution of cane sugar (half sugar, half water), in order to eliminate this difficulty. Each of these additions makes the tint of the lead sulphide slightly paler and less opaque, and thus facilitates the work of comparison.

The effect of iron has been already discussed. In the case of lead glazes, cobalt oxide may have been added to the glaze or dissolved from the body by the glaze. Cobalt salts in alkali sulphide solutions give a dark brown coloration (page 414) which would make the reported amount of lead too high.[2]

To summarise: In order to get reliable results it is necessary that the solutions under comparison have the same general character, otherwise the result may be over 50 per cent. in error. With unknown solutions, this can only be assured by elaborate preparations which occupy much time.

The wide margin of error introduced by differences in the composition of the test and standard solutions can be circumvented by the use of diphenyl-thiocarbazone [3] ("dithizone"). With a number of metals this compound forms intensely coloured complexes which are usually much more readily soluble in organic solvents than in water. Hence, such metals can be extracted from their aqueous solutions by shaking up with a solution of the reagent in a suitable organic solvent, leaving any other salts in the aqueous layer.

Assuming that interfering metals are absent, the solution containing the lead is evaporated to dryness, the residue moistened with a few drops of concentrated hydrochloric acid and then dissolved in the minimum amount of distilled water. If any silica should separate out at this stage it is advisable

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[1] W. Spring, *Bull. Acad. Roy. Belg.*, 483, 1909.

[2] G. D. Elsdon (*Pharm. Journ.*, (4), 89, 143, 176, 1912) points out that in filtering very dilute solutions of lead salts part of the lead may be retained by the filter-paper. If a lead solution be acidified with 0·6 per cent. acetic acid, the adsorption does not occur ; and the lead may be washed from the paper by 0·6 per cent. acetic acid.

[3] H. Fischer and G. Leopoldi, *Wiss. Veröff. Siemens-Konz.*, 12, 44, 1933; *Angew. Chem.*, 47, 90, 1934; F. A. Vorkes and P. A. Clifford, *Journ. Assoc. Off. Agric. Chem.*, 17, 130, 1934; P. A. Clifford and H. J. Wichmann, *ib.*, 19, 130, 1936; E. S. Wilkins, junr., *et al.*, *Ind. Eng. Chem. Anal. Ed.*, 7, 33, 285, 1935; O. B. Winter, *et al.*, *ib.*, 7, 265, 1935; E. B. Sandell, *ib.*, 9, 464, 1937; J. Cholak, *et al.*, *ib.*, 9, 488, 1937; D. M. Hubbard, *ib.*, 9, 493, 1937; A. V. Evlanova, *Journ. App. Chem. (U.S.S.R.)*, 9, 1690, 1696, 1936; W. Weyl and H. Rudow, *Ber. deut. keram. Ges.*, 16, (6), 281, 1935; *Ceram. Abs.* (in *Journ. Amer. Cer. Soc.*, 19, 1936), 15, 27, 1936; G. C. Harold, S. F. Meek and F. R. Holden, *Journ. Ind. Hyg. and Toxic.*, 18, 724, 1936; C. F. Miller, *Chemist-Analyst*, 26, 55, 1937; L. Ellis, *Analyst*, 61, 178, 1936; H. A. Liebhafsky and E. H. Winslow, *Journ. Amer. Chem. Soc.*, 59, 1966, 1937. For other colorimetric processes, see M. R. Moffat and H. S. Spiro, *Chem. Ztg.*, 31, 639, 1907; E. W. Krans and J. B. Ficklen (*Journ. Ind. Hygiene*, 13, 140, 1931) separate the lead as chromate and determine the chromate in acid solution with diphenylcarbazide; S. Feinberg, *Zeit. anal. Chem.*, 96, 415, 1934.

to filter it off. To the solution 5 c.c. of a 10 per cent. sodium citrate solution are added, followed by concentrated ammonia, drop by drop, until the solution is alkaline to litmus; finally an excess of 3 to 4 drops of ammonia is added.

The ammoniacal solution is next extracted in a separating funnel with three successive 10 c.c. portions of a 0·1 per cent. solution of diphenylthiocarbazone in carbon tetrachloride,[1] each extract being washed with an equal bulk of water. If the carbon tetrachloride from the final extraction is not distinctly green in colour, an excess of the reagent is not present and a fourth extraction should be made.

The combined carbon tetrachloride extracts are then extracted twice with 15 to 20 c.c. of a 0·1 per cent. solution of hydrochloric acid, whereby the lead complex is decomposed and the lead passes into the aqueous layer.

The hydrochloric acid extract is made up to a definite volume in a graduated flask and the lead in an aliquot portion of it determined by the sulphide process, as already described.

Alternatively, the lead can be determined colorimetrically by Sandell's procedure as follows:—Pipette out, say, 5 c.c. of the solution into a stoppered test glass, add one drop of a 10 per cent. solution of sodium citrate, 2 drops of 0·88 ammonia solution and 1 c.c. of 5 per cent. potassium cyanide solution. Treat similarly a series of standard lead solutions and to the test and standard solutions add from a burette 2 c.c. of a 0·005 per cent. solution of diphenylthiocarbazone in carbon tetrachloride. Shake the stoppered glasses thoroughly and compare the brick-red colours of the carbon tetrachloride layers in the test and standard solutions by transmitted light against a neutral background.

Bismuth, stannous tin and thallous thallium interfere, as does copper, except in very small amounts. Ferric iron should also be absent as it oxidises the reagent and imparts a yellowish-brown colour to the carbon tetrachloride. It is also obvious that all reagents used must be free from any trace of lead.

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[1] Chloroform is also recommended.

THE DETERMINATION OF BISMUTH AND MERCURY.

§ 168. The Separation of Mercury from Lead, Bismuth, Copper and Cadmium—Rath's Process.

As indicated on page 278, mercuric sulphide is almost insoluble in ammonium sulphide, but readily soluble in sodium or potassium sulphide. If, therefore, the sulphides precipitated by hydrogen sulphide be digested with an alkali sulphide, the mercury will be found with the arsenic and antimony group. Indeed, mercury, tin, arsenic and antimony sulphides can be sharply and conveniently separated from lead, silver, bismuth and copper sulphides by digesting the mixed sulphides in a mixture of potassium sulphide and hydroxide.[1] If cadmium (and zinc) should be present, the mercury sulphide is but imperfectly dissolved.[2] The net result of this operation is a solution containing tin, mercury, arsenic and antimony sulphides, and a precipitate containing copper, lead and bismuth sulphides—assuming that cadmium is absent. If tin also be absent, this method of analysis offers some advantages, because the mercury can be readily separated from the arsenic and antimony by treating the solution with ammonium chloride. If tin be present, much tin will be precipitated with the mercury and the separation by this process is inconvenient.

If the sulphides precipitated by hydrogen sulphide be digested in ammonium sulphide,[3] a good separation can be made in the absence of tin and copper. Mercury, bismuth,[4] lead, copper and cadmium will remain with the insoluble residue, while arsenic and antimony, with some copper sulphide, will be dissolved. If tin be present, a somewhat soluble compound of tin and mercury sulphide appears to be formed, because part of the mercury sulphide will pass into solution and part of the tin will remain with the precipitate.[5]

The plan of analysis must, therefore, be modified to suit these different conditions. Fortunately, mercury is comparatively rare in silicate analysis

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[1] Prepared by saturating half the prepared volume of a 15 per cent. solution of potassium hydroxide with hydrogen sulphide. Mix the two parts, and filter after the solution has stood for some days.

[2] K. Bülow, *Zeit. anal. Chem.*, 31, 697, 1892; *Chem. News*, 67, 174, 1893.

[3] AMMONIUM MONOSULPHIDE.—Saturate three volumes of aqueous ammonia (sp. gr. 0·88) with hydrogen sulphide, and add two volumes of fresh ammonia (sp. gr. 0·88) to the saturated solution. (Ammonium polysulphide is made by dissolving 25 grms. of "flowers of sulphur" in a mixture of 500 c.c. of ammonium monosulphide and 500 c.c. of water.) When mercury is present, the freshly prepared colourless ammonium sulphide is used in place of sodium monosulphide, for the reasons stated on page 278—E. Donath, *Chem. Ztg.*, 15, 1021, 1891.

[4] For the action of hydrogen sulphide on bismuth halides, see E. R. Schneider, *Ann. phys. Chem.*, 93, 464, 1854; M. M. P. Muir and E. M. Eagles, *Journ. Chem. Soc.*, 67, 90, 1895; and on mercuric salts, A. Christensen, *Ber. pharm. Ges.*, 26, 261, 1916; G. McP. Smith and W. L. Semon, *Journ. Amer. Chem. Soc.*, 46, 1325, 1924.

[5] T. Wilm, *Ber.*, 20, 232, 1887.

and one of the two distillation processes indicated later, or simply "loss on ignition" of the original sample, will suffice.   Rath's process [1] is one of the most convenient for separating mercury from the sulphides insoluble in ammonium monosulphide.   It is based on the fact that the mercuric sulphide is insoluble in boiling dilute nitric acid (sp. gr. 1·2–1·3),[2] while the remaining sulphides— silver,[3] bismuth, copper, cadmium and lead—pass into solution.   A little insoluble lead sulphate may be formed by the action of the nitric acid on the sulphide.   The mercuric sulphide can then be separated from the lead sulphate by digesting the mixture with a little aqua regia; dilute the solution with water, filter off the precipitated sulphur and lead sulphate, and wash with water.   A trace of lead sulphate may be dissolved by the acid.   This is recovered later.   The mercury is separated as sulphide by Volhard's process.

§ 169. The Gravimetric Determination of Mercury as Sulphide— Volhard's Process.

In this process [4] the mercury is precipitated as sulphide by the addition of ammonium sulphide to a nearly neutral solution; the mercuric sulphide is dissolved in caustic alkali, from which it is reprecipitated as mercuric sulphide, by the addition of ammonium nitrate.

Precipitation of the Mercuric Sulphide.—Almost neutralise the acid filtrate from the preceding operation with sodium carbonate; add a slight excess of colourless ammonium sulphide (freshly made, page 354); and, finally, with constant agitation, a solution of pure sodium hydroxide.   When the dark colour begins to lighten, heat the solution to boiling, and add more sodium hydroxide until the liquid is perfectly clear.[5]   The mercury dissolves forming a thio-salt—$Hg(SNa)_2$.   Add an excess of ammonium nitrate and boil the solution as long as ammonia is given off.   The thio-salt is decomposed by the ammonium nitrate:

$$Hg(SNa)_2 + 2NH_4NO_3 = 2NaNO_3 + (NH_4)_2S + HgS$$

Wash the precipitated mercuric sulphide [6] by decantation through a dried and weighed Gooch crucible two or three times with hydrogen sulphide water, then with hot water until the water no longer reacts with silver nitrate.   Transfer the precipitate to the crucible, dry between 110° and 112°,[7] and weigh as

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[1] G. von Rath, *Pogg. Ann.*, **96**, 322, 1855.

[2] J. Torrey, *Amer. Chem. Journ.*, **7**, 355, 1886; J. L. Howe, *ib.*, **8**, 75, 1886.   Mercuric sulphide is not appreciably attacked by boiling dilute nitric acid, but a single drop of dilute hydrochloric acid (1 : 3) will convert black mercuric sulphide into a yellow compound, and if a few drops of hydrochloric acid be present, some of the mercury will pass into solution.   Hence the nitric acid must be perfectly free from chlorides and hydrochloric acid.

[3] If silver be present, it will be precipitated as chloride by any hydrochloric acid present.

[4] J. Volhard, *Liebig's Ann.*, **255**, 255, 1889; E. T. Allen and J. L. Crenshaw, *Zeit. anorg. Chem.*, **79**, 125, 1913.

[5] A precipitate of insoluble lead sulphate may be present owing to the dissolution of some lead sulphate in the aqua regia.   If present, it must be filtered off and the precipitate washed with dilute sodium hydroxide.   The lead sulphate is mixed with that previously obtained and treated by the method of page 326.

[6] The precipitate so obtained is much more compact and easily filtered than mercuric sulphide precipitated by hydrogen sulphide.   Moreover, the precipitate produced by hydrogen sulphide in acid solutions weighs too heavy, particularly if iodides are present.—W. Reinders, *Zeit. phys. Chem.*, **32**, 498, 1900; C. J. Pretzfeld, *Journ. Amer. Chem. Soc.*, **25**, 198, 1903; F. Dunning and L. H. Farinholt, *ib.*, **51**, 804, 1929; I. B. Johns, W. D. Peterson and R. M. Hixon, *ib.*, **52**, 2820, 1930; E. P. Fennimore and E. C. Wagner, *ib.*, **53**, 2453, 1931; H. Wegelius and S. Kilpi, *Zeit. anorg. Chem.*, **61**, 413, 1909.

[7] The time of drying is materially lessened by a final washing with alcohol—R. S. M'Bride, *Journ. Phys. Chem.*, **14**, 189, 1910.

mercuric sulphide—HgS. Every gram of the mercuric sulphide represents 0·8622 gram of mercury, or 0·9309 gram mercuric oxide—HgO. The results are generally a little high owing to the presence of some sulphur with the precipitate.[1]

Removal of Sulphur from Metallic Sulphides.—The sulphur may be removed either by boiling the precipitate with a little sodium sulphite before filtering so as to convert the sulphur into soluble sodium thiosulphate $(S + Na_2SO_3 = Na_2S_2O_3)$, or by extraction with carbon disulphide.[2] Conversely, the mercuric sulphide can be extracted from the dry, weighed mixture by cold,
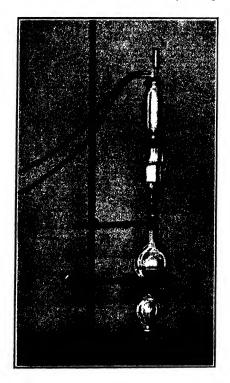
Fig. 94.—Extraction Apparatus.

concentrated hydriodic acid and the residue of sulphur weighed.[3] The following are convenient methods of conducting the process of extraction:—The Gooch crucible containing the mixture is placed on a glass tripod whose feet rest on the bottom of a beaker containing some carbon disulphide. The beaker is covered with a round-bottomed flask containing cold water. The beaker is placed on a hot-water bath.[4] The carbon disulphide boils at 46° and,

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[1] F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, **2**, 140, 1911; L. Vignon, *Compt. rend.*, **116**, 584, 1893.

[2] C. Friedheim and P. Michaelis, *Zeit. anal. Chem.*, **34**, 526, 1895; H. W. Wiley, *ib.*, **23**, 586, 1884; G. Vortmann, *Uebungsbeispiele aus der quantitativen chemischen Analyse*, Leipzig, 33, 1910. For the use of tri-, tetra- or penta-chloroethylene in place of carbon disulphide, see F. Utz, *Gummi Zeit.*, **28**, 126, 1913; for alcohol, P. Wenger and M. Schilt, *Helv. Chim. Acta*, **7**, 907, 1924.

[3] E. R. Caley and M. G. Burford, *Ind. Eng. Chem. Anal. Ed.*, **8**, 43, 1936.

[4] Note, no naked flames must be near enough to risk ignition of the carbon disulphide.

after condensing against the bottom of the flask, drops into the crucible and passes back to the bottom of the beaker.   Wiley's or Drehschmidt's extraction apparatus [1] is convenient for washing precipitates free from sulphur by extraction with carbon disulphide.   Both have a receptacle, A, for the Gooch crucible below a condenser, C; Drehschmidt's is shown in fig. 94.   A current of cold water is passed through the condenser, and the flask, B, containing the solvent is placed in a hot-water bath, or supported over an incandescent electric lamp.   The carbon disulphide boils and the condensed liquid runs through the crucible back to the bottom of the flask.   In about half an hour the apparatus is allowed to cool and the carbon disulphide is washed from the precipitate in the crucible by one treatment with alcohol and one treatment with ether.   Dry the sulphide at 110° and weigh as indicated above.   The results are very fair, generally less than 0·1 per cent. low.

§ 170. The Distillation Process for Mercury.

Erdmann and Marchand's Process.

All mercury compounds, with the exception of the iodide, are quantitatively decomposed when heated with quicklime.[2]   The reaction, in the case of the chloride, is represented:

$$HgCl_2 + CaO = CaCl_2 + HgO$$

Hence it is often most convenient to determine the mercury on a separate sample by a distillation process, and ignore the mercury when the other constituents are determined, because the mercury compound which might contaminate a precipitate is volatilised when the precipitate is ignited before weighing.[3]

Mercury can be determined in colours containing, say, mercuric chromate, and in gold amalgams and "best" gold, by placing a plug of asbestos at the end of a combustion tube—45 to 50 cm. long and 1·5 cm. wide—then an 8 cm. layer of freshly ignited calcium oxide; a 10 cm. layer of an intimate mixture of a weighed quantity of the given substance with an excess of calcium oxide; a 20 cm. layer of calcium oxide; and, finally, a loose plug of asbestos fibre. Bend the end of the tube, adjacent to the longer layer of calcium oxide, as shown in the diagram at C, fig. 95.   Connect the bent end of the combustion tube, by means of a piece of rubber tubing, with one arm of a small, weighed Péligot's tube, B.   The other arm of the Péligot's tube, D, is loosely packed with pure gold leaf.   The rear end of the combustion tube is connected with a wash-bottle, A, containing sulphuric acid, and with a tube delivering coal-gas. The coal-gas is allowed to bubble through the apparatus at the rate of about three bubbles per second for about half an hour.   Gradually raise the temperature of the fore end of the combustion tube and slowly carry the flame backwards until finally the whole tube is being heated at the same time.   If necessary, the part C of the combustion tube is heated with a naked Bunsen flame, so that any mercury condensed here is driven forward into the Péligot's

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[1] H. W. Wiley, *Journ. Anal. App. Chem.*, **7**, 65, 1893; W. D. Richardson and E. F. Scherubel, *Journ. Ind. Eng. Chem.*, **4**, 220, 1912; H. J. C. Curr, *ib.*, **4**, 535, 1912; K. Neumann and R. von Spallart, *Chem. Ztg.*, **40**, 981, 1916.

[2] O. L. Erdmann and R. F. Marchand, *Journ. prakt. Chem.*, (1), **31**, 385, 1844; C. R. König, *ib.*, (1), **70**, 64, 1857.   H. Rose (*Ann. phys. Chem.*, (2), **110**, 542, 1860) showed that accurate results are obtained with mercuric iodide if finely powdered copper is added to the mixture of mercury salt and lime. J. J. Fahey, *Ind. Eng. Chem. Anal. Ed.*, **9**, 477, 1937.

[3] A simple determination of the "loss on ignition" is sometimes sufficient for the mercury in a dry sample of mercury chromate.   The last trace of mercury is difficult to expel from gold—M. J. Personne, *Compt. rend.*, **56**, 63, 1862.

tube, but the rubber connection must not be scorched. The current of coal-gas is continued all the time the combustion is in progress and while the apparatus is cooling. Most of the mercury collects in the lower bulb of the Péligot's
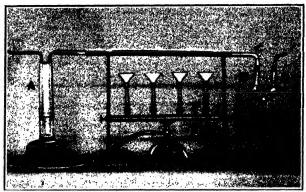

FIG. 95.—Erdmann and Marchand's Distillation Process for Mercury.

tube; a small part is arrested by amalgamation with the gold leaf[1]; and some of the mercury may still remain in the bent portion of the combustion tube near C. The Péligot's tube is disconnected [2] and a current of air, dried by passing through a drying tower, fig. 122, is passed through it for about half an hour. Weigh the Péligot's tube: the increase in weight represents mercury derived from the given sample. Now cut the combustion tube where the mercury is condensed. Dry with air and weigh. Heat this portion of the combustion tube while a current of air is passed through. This volatilises the mercury. Cool the tube in a desiccator and weigh again. The apparent loss in weight represents the mercury which was condensed in the tube. Add this to the preceding result to get the total mercury.[3]

Holloway's Modification of Eschka's Process.

This method is based on the fact that when mercuric sulphide is heated with iron filings, iron sulphide and volatile mercury are formed.[4] The mercury is condensed on a gold or silver plate, and an amalgam is formed. The increase in the weight of the plate from this cause represents the amount of mercury in the sample. The process is used for sulphides and amalgams. The process can also be used with "best gold" and similar amalgams.[5]

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[1] Instead of using gold leaf, the mercury is sometimes condensed in a layer of water, placed in the bottom of the Péligot's tube. In this case the rear end of the combustion tube is sealed and the closed end packed with magnesite or sodium bicarbonate, which, on heating towards the end of the operation, evolves a stream of carbon dioxide; this drives out the mercury vapour. The results are satisfactory with rich (7–8 per cent. mercury) ores.

[2] Watch that no mercury falls from the combustion tube after the Péligot's tube has been disconnected.

[3] Many modifications have been described. See A. C. Cumming and J. Macleod (*Journ. Chem. Soc.*, 103, 513, 1913) for a modification based on Penfield's process for the determination of water in minerals (page 641). When the substance contains organic matter, the condensed mercury is apt to be contaminated with a tarry or crystalline distillate. In such cases J. E. Marsh and O. G. Lye (*Analyst*, 42, 84, 1917) mix the mercury compound with twice its weight of calcium sulphate and then mix with excess of lime.

[4] As in Jordan's test for mercury—W. J. Jordan, *Schweigger's Journ.*, 57, 339, 1829.

[5] A. Eschka, *Chem. News*, 26, 22, 1872; *Zeit. anal. Chem.*, 11, 344, 1872; *Dingler's Journ.*, 204, 47, 1872; C. T. Holloway, *Analyst*, 31, 66, 1906; *Chem. Eng.*, 4, 169, 1906; R. E. Chism, *Eng. Min. Journ.*, 66, 480, 1898; G. A. James, *ib.*, 90, 800, 1910; S. Piña de Rubies, *Anal. Fis. Quim.*, 16, 661, 1918; W. W. Whitton, *California Journ. Tech.*, 4, 23, 1904.

The Apparatus.—The upper edge of a deep, glazed porcelain crucible—about 4 cm. diameter, and 4·5 cm. high—is ground flat. The crucible, *A*, fig. 96, is supported in a hole in an asbestos or silica plate, *H*. A disc of silver [1] plate, 5 cm. in diameter (weighing about 0·4–0·5 grm. per sq. cm.) is annealed by holding it in the Bunsen flame for a minute or two. The disc is rubbed between two flat surfaces until it lies perfectly flat on top of the crucible. Weigh this disc, *B*. Place a rather larger metal disc, *C*, on top of the weighed disc in order to keep the latter clean.
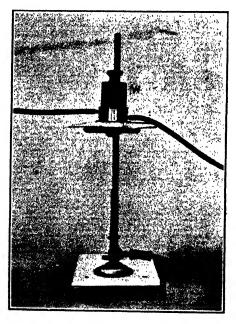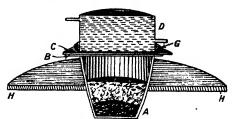

FIG. 96.—Holloway's Apparatus.

A metal condenser, *D*, through which a current of cold water is flowing, is placed on the discs to keep them cool. The condenser is held in place by a 500 grm. weight, *W*, fig. 97, on top of the condenser. A gutter, *G*, runs round the bottom of the condenser to collect any condensed moisture trickling down the condenser. The moisture is removed from time to time by means of a piece of blotting-paper.

Charging the Crucible.—The finely powdered (120's lawn) and dry [2] sample is weighed [3] into the crucible and mixed with 10 grms. of fine iron filings.[4] The mixture is covered with 5 grms. of the coarse iron filings. Everything is placed in position, as shown in the diagrams, figs. 96 and 97.

Volatilisation of the Mercury.—The crucible is heated with a small flame [5] sufficient to raise the bottom to redness without the flame coming in contact with the sides. After heating from 20 to 30 minutes, let the system cool for 15 minutes with the condenser at work to guard

FIG. 97.—Holloway's Apparatus.

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[1] Gold has a greater affinity for the mercury than silver; but silver has the greater "collecting" power weight for weight and is also a better heat conductor. Hence Holloway recommended silver; Eschka and Chism used gold.

[2] If metallic mercury be present, the drying must be conducted with care on account of the tendency of mercury to volatilise.

[3] If the amount of mercury in the sample is less than 1 per cent., take 2 grms. of the sample; if between 1 and 2 per cent., take 1 grm.; if between 2 and 5 per cent., take 0·5 grm.; and if over 5 per cent. is present, grind the sample with 10 grms. of dry sand (120's lawn) and take an aliquot portion so as to keep approximately within the indicated limits.

[4] Clean iron filings free from oils and fats are prepared by heating the filings to redness for an hour in a covered crucible. Sift the filings through an 80's lawn, and also sift some through a 30's lawn. Keep each in a separate bottle.

[5] The tip of a small Méker's flame is very suitable. The plate does not absorb mercury well if it is hot.

against the loss of uncondensed mercury vapour. Wash the gold or silver disc with alcohol[1]; dry in a desiccator; and weigh. The increase in weight of the disc represents the mercury. It requires a little practice to adjust the size of the flame and the time of heating in order to be sure all the mercury is volatilised under the conditions just indicated.[2] To make quite sure, reheat the crucible with a fresh gold or silver disc in position. If all the mercury was volatilised during the first heating, there will be no increase in weight of the disc. If any increase in weight is obtained, add the result to the mercury obtained with the first plate. The plates can be freed from mercury, and prepared for another determination, by simply heating them to drive off the mercury.[3] A determination occupies 40 to 50 minutes.

Special Precautions.—(1) Avoid excessive heating of the crucible; the edge of the disc should never feel warm to the fingers. (2) The gold or silver disc should be thoroughly cleaned and fit on the crucible quite flat. (3) The disc and cooler should be carefully adjusted to ensure contact all round the top of the crucible. (4) The disc should be quite dry. (5) Draughts are objectionable. (6) Allow 15 minutes for cooling before removing the disc to prevent danger of losing uncondensed mercury vapour.

Duplicate determinations on a 1 per cent. ore should agree to within 0·05 per cent. (Holloway), a result which cannot be equalled by the wet method.

A variety of volumetric and electrolytic methods has also been described for the determination of mercury.[4]

§ 171. The Separation of Bismuth from Lead, Cadmium and Copper—Löwe's Process.

Löwe [5] has based a process on the fact that water converts bismuth nitrate into an insoluble basic salt under conditions where lead, copper and cadmium salts undergo no such transformation:

$$Bi(NO_3)_3 + 2H_2O \rightleftharpoons Bi(OH)_2NO_3 + 2HNO_3$$

Hence the process can be used for the separation of bismuth from the

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[1] To remove tarry and organic matters which may have collected on the gold or silver plate. The gold amalgams used in pottery, if already mixed with "fat oil," should be washed with ether to remove the oil before treatment by this process.

[2] If the plate does not show a clear circular stain, either too much ore has been used or the lid did not fit properly. If the stain extends beyond the edge of the crucible, there will be an element of uncertainty owing to the probable loss of mercury. The plate and crucible should fit close enough to prevent this.

[3] The plate seems to improve with use, since it gets more porous and absorbs mercury better.

[4] For a discussion of volumetric methods, see H. B. Dunnicliff and H. D. Suri, *Analyst*, **54**, 405, 1929; M. L. Colombier, *Journ. Pharm. Chim.*, (7), **10**, 15, 1929. For electrolytic processes, see E. F. Smith, *Electro-Analysis*, Philadelphia, 99, 223, 1918; S. Lomholt and J. A. Christiansen, *Biochem. Zeit.*, **55**, 216, 1913; *ib.*, **81**, 356, 1917; J. Guzmán and P. Poch, *Anal. Fis. Quim.*, **16**, 742, 1918; W. Böttger, *Zeit. angew. Chem.*, **34**, 120, 1921; A. de Mecús, *Bull. Soc. chim. Belg.*, **31**, 302, 1922; A. Stock and R. Heller, *Zeit. angew. Chem.*, **39**, 466, 1926; A. Verdino, *Mikrochem.*, **6**, 5, 1928. For a review of recent work on the determination of mercury, see W. Fischbach, *Zeit. anal. Chem.*, **96**, 436, 1934.

[5] J. Löwe, *Journ. prakt. Chem.*, (1), **74**, 344, 1858; C. H. Pfaff, *Handbuch der analytischen Chemie*, Altona, 1921; G. Luff, *Zeit. anal. Chem.*, **63**, 330, 1923; *Chem. Ztg.*, **44**, 71, 1920; P. P. Solodovnikov, *Uchenuie Zapiski Kazan Gosudarst. Univ.*, **88**, 457, 1928. This process can be used for evaluating bismuth nitrate and bismuth oxide. The latter is soluble in nitric acid. For the determination of bismuth with gallic acid, see L. Kieft and G. C. Chandlee, *Ind. Eng. Chem. Anal. Ed.*, **8**, 392, 1936.

elements just named. The basic nitrate is washed with a solution of ammonium nitrate; this allows the precipitate to be washed without decomposition. If water alone be used, the precipitate becomes more and more basic, the filtrate consequently acquires an acid reaction and some bismuth passes into solution.

Precipitation.—The nitric acid solution of the sulphides is evaporated on a water bath to a syrupy consistency, mixed with hot water and thoroughly stirred with a glass rod. Take care to loosen any crusts which may have formed on the sides of the basin. The solution is again evaporated and the addition of water and the evaporation are repeated until further addition of water produces no turbidity—three or four evaporations usually suffice. This shows that the reaction indicated above is complete. Evaporate the solution to dryness and, when the dry mass has ceased to smell of nitric acid, cool.

Washing.—Add a cold solution of ammonium nitrate (2E) and, after standing some time with frequent agitation to make sure that all the lead nitrate has passed into solution, filter. Wash the precipitate with the solution of ammonium nitrate and dry in an air bath.

Ignition.—Remove the dry precipitate from the filter-paper and transfer it to a watch-glass. Ignite the filter-paper in a porcelain crucible at a low temperature. Moisten the ash with nitric acid. Evaporate to dryness very cautiously to prevent spurting. Transfer the precipitate to the crucible and ignite filter-paper ash and precipitate together. Try to keep the temperature below the fusing point of the oxide (c. 820°), since, if the temperature be too high, the oxide melts and attacks the glaze.[1] When the weight has become constant, weigh the precipitate as bismuth oxide—Bi_2O_3.

Purification of the Bismuth Oxide.—The precipitate may be contaminated with a little iron, mercury and copper if these elements be present. Hence some prefer to redissolve the precipitate before ignition and repeat the separation. The combined filtrates are evaporated to dryness and calcined at a low temperature to destroy the ammonium salts, which interfere with the subsequent precipitation of the lead as sulphate (page 326).

If sulphuric or hydrochloric acid be present, a basic sulphate or chloride may be formed, which is not converted to oxide on ignition.[2] The results will accordingly be high. In that case, Rose[3] recommends fusing the mass for about 15 minutes with four or five times its weight of, say, 98 per cent. potassium cyanide in a covered crucible. When all is fused, the crucible is gently rotated to collect the little beads of metal into one button. The crucible should not be heated above low redness. Wash the cold mass with water to remove the cyanides and cyanates. The button is then washed with alcohol, dried at 100° and weighed as metallic bismuth. This weight multiplied by 1·1148 gives the corresponding amount of bismuth oxide—Bi_2O_3.[4]

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[1] The error from this cause can be neglected in most cases. If reducing gases be present inside the crucible, some of the oxide will be partially reduced.

[2] For the determination of bismuth as oxychloride, see O. A. Crickett, *Eng. Min. Journ.*, **112**, 58, 1921; J. Antal, *Gyógysz Dokt. Diss.*, Budapest, 1928; W. Hertel, *Met. u. Erz*, **27**, 557, 1930; as oxybromide, L. Moser and W. Maxymowicz, *Zeit. anal. Chem.*, **67**, 248, 1925; as oxyiodide, R. Strebinger and W. Zins, *Mikrochem.*, **5**, 166, 1927; *Zeit. anal. Chem.*, **72**, 417, 1927; R. Strebinger and G. Ortner, *ib.*, **107**, 14, 1936.

[3] H. Rose, *Pogg. Ann.*, **91**, 104, 1854; **110**, 136, 426, 1860.

[4] Sometimes the bismuth forms a kind of metallic lustrous film inside the crucible. For the precipitation of bismuth as metal, see L. Vanino and F. Treubert, *Ber.*, **31**, 1303, 1898; E. Rupp and G. Hamann, *Zeit. anal. Chem.*, **87**, 32, 1931.

§ 172. The Separation of Bismuth from Copper and Cadmium— Jannasch's Process.

The bismuth can be separated [1] from copper and cadmium, if cadmium be present, by evaporating a solution containing salts of these elements to dryness. Dissolve the residue in, say, 5 c.c. of nitric acid (sp. gr. 1·4) and 25 c.c. of water, and pour the solution into a beaker containing 25 c.c. of concentrated ammonia and 50 c.c. of a 4 per cent. solution of hydrogen peroxide, with constant stirring. A dull yellow precipitate of bismuth hydroxide separates.[2] Let the precipitate settle; decant the clear liquid; add more of the ammoniacal hydrogen peroxide; decant; transfer to a filter-paper; wash with hot dilute ammonia (1 : 8), and finally with hot water, until a drop of the wash-water gives no residue when evaporated on a piece of platinum foil.

To remove any copper or cadmium which might be precipitated with the bismuth, dissolve the precipitate on the filter-paper in hot dilute nitric acid; evaporate to dryness and repeat the precipitation as described above.

After complete washing, dry the precipitate at 90°–95°; ignite it in a porcelain crucible until its weight is constant; and weigh as Bi_2O_3. The ignition of the precipitate and paper is described in detail on page 361.[3]

§ 173. The Determination of Bismuth Colorimetrically.

Small amounts of bismuth are conveniently determined colorimetrically. Bismuth triiodide [4] dissolves in excess of potassium iodide, forming an intense yellow, orange or red coloration [5] which, unlike the somewhat similar colour given by iodine, is not destroyed by sulphurous acid.

The colorimetric process for bismuth has recently been subjected to close scrutiny in connexion with the determination of traces of bismuth in copper.[6] The following scheme has been adapted from this work to the case of ceramic materials. If present, arsenic, antimony and tin, mercury and lead are separated by the processes given on pages 276, 354, 326 respectively. Bismuth

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[1] P. Jannasch and J. Leskinsky, *Ber.*, **26**, 2908, 1893; P. Jannasch and E. Rose, *ib.*, **27**, 2227, 1894; P. Jannasch and E. von Cloedt, *ib.*, **28**, 994, 1895; *Chem. News*, **72**, 64, 1895; P. Jannasch, *Zeit. anorg. Chem.*, **8**, 302, 1895; *Leitfaden der Gewichtsanalyse*, Leipzig, 107, 110, 1904; P. P. Solodovnikov, *Uchenuie Zapiski Kazan Gosudarst. Univ.*, **88**, 457, 1928.

[2] If lead were present, it too would be precipitated with the bismuth as a peroxide.

[3] A. L. Benkert and E. F. Smith's process (*Journ. Amer. Chem. Soc.*, **18**, 1055, 1896; A. F. V. Little and E. Cahen, *Analyst*, **35**, 301, 1910), by precipitation as bismuth formate, is an excellent process for the separation of bismuth from lead and cadmium.

[4] F. Field, *Chem. News*, **36**, 260, 1877; F. A. Abel and F. Field, *Journ. Chem. Soc.*, **14**, 290, 1862; M. Planes, *Chem. News*, **89**, 10, 1904; *Journ. Pharm. Chim.*, (6), 385, 1903; L. L. de Koninck, *Bull. Soc. chim. Belg.*, **19**, 91, 1905; F. B. Stone, *Journ. Soc. Chem. Ind.*, **6**, 416, 1887; T. C. Cloud, *ib.*, **23**, 523, 1904; H. A. B. Motherwell, *Eng. Min. Journ.*, **104**, 1091, 1917; C. O. Jones and E. C. Frost, *Ind. Eng. Chem.*, **18**, 596, 1926; P. Dumont and M. Bouillenne, *Compt. rend. Soc. biol.*, **99**, 1247, 1928; *Chem. Zentr.*, (1), 562, 1929; C. Frick and H. Engemann, *Chem. Ztg.*, **53**, 505, 601, 1929; N. Kameyana and S. Makishima, *Journ. Soc. Chem. Ind. Japan*, **36**, (Suppl. binding), 364, 1933; A. Portnov and V. Skvorzov, *Farm. Zhur.*, 534, 1928; *Chem. Zentr.*, (1), 114, 1929; L. A. Haddock, *Analyst*, **59**, 163, 1934.

[5] One part of bismuth per 10,000 parts of water gives an orange colour; 1 part of bismuth in 40,000 parts of water, a light orange; and 1 part of bismuth in 100,000, a perceptible yellow coloration—T. C. Thresh, *Pharm. Journ.*, **10**, 641, 1880; *Journ. Chem. Soc.*, **38**, 752, 1880.

[6] A. J. G. Smout and J. L. Smith, *Chem. Trade Journ.*, **92**, 420, 1933; *Analyst*, **58**, 475, 1933.

is then separated from copper and cadmium by Jannasch's method (page 362). Since only traces of bismuth are present, it is necessary to have at this stage a sufficient quantity of another element present to ensure that the whole of the bismuth is precipitated. Hence add about 0·025 grm. of ferrous ammonium sulphate for every gram of analysis sample taken. Reprecipitation of the mixed hydroxides of bismuth and iron is essential to remove the last traces of copper (and cadmium). The solution in both the initial and final precipitations should be stood for at least six hours in a warm place, as the complete precipitation of bismuth takes a considerable time. The final precipitate is dissolved in dilute sulphuric acid, the solution just neutralised and then again made faintly acidic. The iron is now reduced to the ferrous state by the addition of a slight excess of sulphurous acid,[1] about 10 c.c. of a 2 per cent. solution of potassium iodide are added and the solution made up to a definite volume. The final solution is matched against a blank solution which has been prepared by carrying through all the above analytical operations from the initial precipitation of the mixed hydroxides. Into the blank solution a standard solution of bismuth [2] is run until the colours match. In the final solutions the acidity should be about 2 per cent. by volume and the amount of potassium iodide solution added should be adequate but not excessive. The dilution of the test solution should be such that not more than 4 to 5 c.c. of standard bismuth solution are needed for a match. The method is said to be reliable from 0·002 to 0·020 per cent. of bismuth.[3]

Bismuth can also be determined as phosphate,[4] or by metallic displacement from solution. The precipitated bismuth is allowed to interact with a ferric salt, followed by titration of the ferrous salt formed in the reaction: [5]

$$Bi + 3FeCl_3 = BiCl_3 + 3FeCl_2$$

The use of organic precipitants has also been advocated.[6]

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[1] Haddock (*l.c.*) adds also 2 c.c. of 30 per cent. hypophosphorous acid.

[2] STANDARD BISMUTH SOLUTION.—Dissolve 0·0897 grm. of pure bismuth in 20 c.c. of concentrated sulphuric acid and dilute to a litre. One c.c. of this solution is equivalent to 0·0001 grm. Bi_2O_3.

[3] The coloured complexes formed between bismuth iodide and organic compounds have been used for quantitative work—P. Aubry, *Journ. Pharm. Chim.*, (7), **25**, 15, 1922; L. Cuny and G. Poirot, *ib.*, (7), **28**, 215, 1923; C. E. Laporte, *ib.*, (7), **28**, 304, 1923; A. Girard and E. Fourneau, *Compt. rend.*, **181**, 610, 1925. For a volumetric process based on the formation of bismuth iodide, see C. Reichard, *Pharm. Zentrh.*, **54**, 103, 1913. H. Heinrichs and M. Hertrich (*Glastech. Ber.*, **2**, 112, 1924) determine bismuth colorimetrically with ammonium thiocyanate, as in the corresponding process for iron. C. Mahr (*Zeit. anal. Chem.*, **94**, 161, 1933; **97**, 96, 1934) has worked out a process, based on the colour given by bismuth salts with thiourea, which is applicable in the presence of silver, lead, copper and ferrous iron—compare G. Sensi and S. Seghezzo, *Ann. Chim. appl.*, **19**, 392, 1929; L. A. Haddock, *Analyst*, **59**, 163, 1934.

[4] W. R. Schoeller and E. F. Waterhouse, *Analyst*, **45**, 435, 1920; W. R. Schoeller and D. A. Lambie, *ib.*, **62**, 533, 1937; G. Luff, *Chem. Ztg.*, **47**, 133, 1923; G. G. Reissaus, *Zeit. anal. Chem.*, **70**, 300, 1927; H. Blumenthal, *ib.*, **78**, 206, 1929; P. Farini, *Boll. Chim. Farm.*, **73**, 284, 1934; W. C. Blasdale and W. C. Parle, *Ind. Eng. Chem. Anal. Ed.*, **8**, 352, 1936.

[5] A. K. Kurtenacker and F. Werner, *Zeit. anorg. Chem.*, **123**, 166, 1922; J. Hanus and A. Jílek, *Chem. Listy*, **18**, 8, 1924; G. G. Reissaus (*v. supra*); W. Strecker and A. Herrmann, *Zeit. anal. Chem.*, **72**, 5, 1927; H. Kubina and J. Plichter, *ib.*, **72**, 201, 1927; G. J. Hough, *Chemist-Analyst*, **18**, 3, 1929.

[6] R. Berg and O. Wurm, *Ber.*, **60B**, 1664, 1927; R. Berg, *Zeit. anal. Chem.*, **72**, 177, 1927; G. Spacu and G. Suciu, *ib.*, **79**, 196, 1929; A. Pinkus and J. Dernies, *Bull. Soc. chim. Belg.*, **37**, 267, 1928; P. Farini, *Boll. Chim. Farm.*, **73**, 284, 1934.

A number of electrolytic methods have been proposed for the determination of bismuth, though none has gained wide acceptance.[1]

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[1] See, for instance, G. Vortmann, *Ber.*, **24**, 2749, 1891 ; D. Balachowsky, *Compt. rend.*, **131**, 179, 1900; A. Lassieur, *ib.*, **179**, 632, 1924; K. Wimmenauer, *Zeit. anorg. Chem.*, **27**, 1, 1901; B. P. Richardson, *ib.*, **84**, 277, 1913; A. L. Kammerer, *Journ. Amer. Chem. Soc.*, **25**, 83, 1903; B. L. Murray, *Journ. Ind. Eng. Chem.*, **8**, 257, 1916; P. Poch, *Anal. Fis. Quim.*, **16**, 520, 1918; M. Nakao, *Journ. Pharm. Soc. Japan*, No. 446, 275, 1919; K. Seel, *Zeit. angew. Chem.*, **37**, 541, 1924; A. Jilek and J. Lukas, *Coll. Czech. Chem. Comm.*, **1**, 369, 1929; E. P. Schoch and D. J. Brown, *Eighth Inter. Cong. App. Chem.*, **21**, 81, 1912; R. C. Benner, *ib.*, **21**, 91, 1912.

CHAPTER XXVI.

THE DETERMINATION OF COPPER AND CADMIUM.

§ 174. Rivot's Thiocyanate Process for the Separation of Copper from Cadmium.

IF cadmium be absent, copper is sometimes precipitated by hydrogen sulphide,[1] or by aluminium (page 371), as well as electrolytically. The main objections to the former process are the time needed for a complete precipitation and the tendency of the precipitated sulphide to oxidise and form soluble copper sulphate by exposure to air during the washing on the filter-paper; nor is the use of hydrogen sulphide an attractive feature of the process. Kern and Morris [2] compared the results obtained by precipitating copper with hydrogen sulphide and with aluminium and found that "the precipitation by aluminium gave as accurate results as when made by means of hydrogen sulphide." There is also a difficulty in igniting copper sulphide and weighing it as such.[3] The very valuable electrolytic process for copper, described on page 255, will not work in the presence of cadmium. If cadmium be present, Rivot's process [4] suggested in 1854 may be used. This depends upon the fact that an alkali thiocyanate produces a precipitate of cuprous thiocyanate—CuCNS— in neutral or feebly acid solutions of a copper salt in the presence of a reducing agent—say sulphurous or hypophosphorous acid. The solution is best slightly acidified with sulphuric or hydrochloric acid. An excess of acid is

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[1] J. B. Coppock, *Chem. News*, **73**, 262, 1896; B. Brauner, *ib.*, **74**, 99, 1896; J. Thomsen, *Ber.*, **11**, 2043, 1878. For a survey of methods for the determination of copper, see W. B. Price *et al.*, *Journ. Ind. Eng. Chem.*, **7**, 546, 1915; H. W. Foote and J. E. Vance, *ib.*, *Anal. Ed.*, **9**, 205, 1937.

[2] E. F. Kern and M. H. Morris, *School Mines Quart.*, **35**, 1, 1914.

[3] R. Wegscheider, *Monats.*, **14**, 315, 1893; C. Beck, *Chem. Ztg.*, **37**, 1330, 1913; E. Murmann, *Chem. Zentr.*, (1), 2016, 1914; F. L. Hahn, *Zeit. anorg. Chem.*, **99**, 201, 1917; *Zeit. anal. Chem.*, **65**, 134, 1924; *Ber.*, **63B**, 1616, 1930; E. Wilke-Dörfurt and U. Rhein, *Zeit. anal. Chem.*, **64**, 380, 1924; M. Leo, *Chem. Ztg.*, **48**, 841, 1924.

[4] L. E. Rivot, *Compt. rend.*, **38**, 868, 1854; R. G. van Name, *Amer. Journ. Sci.*, (4), **10**, 451, 1900; **13**, 20, 138, 1902; E. Busse, *Zeit. anal. Chem.*, **17**, 53, 1878; **30**, 122, 1891; H. Tamm, *Chem. News*, **24**, 91, 1874; E. Fleischer, *ib.*, **19**, 206, 1869; G. Fernekes and A. A. Koch, *Journ. Amer. Chem. Soc.*, **27**, 1224, 1905; W. Hampe, *Chem. Ztg.*, **17**, 1691, 1893; *Journ. Soc. Chem. Ind.*, **13**, 421, 1894; B. Blount, *Analyst*, **19**, 92, 1894; D. J. Demorest, *Journ. Ind. Eng. Chem.*, **5**, 215, 1913; L. von Wissell and F. Küspert, *Landw. Vers. Stat.*, **86**, 277, 1915; I. M. Kolthoff and G. H. P. van der Meene, *Zeit. anal. Chem.*, **72**, 337, 1927; D. Krüger and E. Tschirch, *ib.*, **97**, 161, 1934; W. Hiltner and W. Grundmann, *ib.*, **97**, 172, 1934. For the separation of copper and cadmium by precipitating the copper by a moderate excess of potassium iodide, evaporating to dryness, extracting with water, filtering and drying the separated cuprous iodide at 120°–150°, see P. E. Browning, *Amer. Journ. Sci.*, (3), **46**, 280, 1894; L. W. Winkler, *Zeit. anal. Chem.*, **63**, 324, 1923; I. M. Kolthoff and H. A. Kuyl- man, *Chem. Weekblad*, **23**, 185, 1926. The cadmium in the filtrate is subsequently precipitated by sodium carbonate and ignited to CdO. For the separation of copper and iron, see G. Edgar, *Journ. Amer. Chem. Soc.*, **38**, 884, 1916.

injurious. The solution should be free from oxidising agents—*e.g.* nitric acid, free chlorine oxides. The process enables copper to be quantitatively separated from cadmium and, indeed, many other metals.[1]

The Precipitation.—The solution [2] is neutralised with ammonia, if necessary, acidified with a couple of drops of sulphuric acid and treated with an excess of sulphur dioxide or ammonium bisulphite.[3] Then add, drop by drop with constant stirring, an aqueous solution of ammonium thiocyanate. The greenish precipitate of mixed cuprous and cupric thiocyanates soon becomes white. Let the mixture stand overnight.

Washing and Drying the Precipitate.—Filter the solution, with the bulky precipitate, through a Gooch crucible, previously dried at 120° and weighed; wash with cold water [4] until the washings give but a faint red coloration with a solution of ferric chloride.[5] Then wash six times with 20 per cent. alcohol. Dry the precipitate between 110° and 120°; and weigh as CuCNS. The drying must be repeated until the weight is constant.[6] The weight of the precipitate multiplied by 0·6542 gives the corresponding amount of cupric oxide—CuO.

Accuracy of the Results.—The results are excellent. For example, with known amounts of copper, Fernekes and Koch found:

| Copper (taken) | . | . | 0·0939 | 0·0939 | 0·0939 | 0·0188 | 0·0188 grm. |
| Copper (found) | . | . | 0·0941 | 0·0939 | 0·0939 | 0·0189 | 0·0188 grm. |

The main objections to the method are the slight solubility of the precipitate in an excess of the precipitating reagent,[7] and in water; and the tardy separation of the precipitate. The method can be used to separate copper from zinc,

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[1] Copper may also be separated from cadmium (also Pb, Mg, Mn, Hg, Zn) by the nitroso-β-naphthol process, as indicated on page 420—G. von Knorre, *Zeit. anal. Chem.*, 28, 234, 1889; and from cadmium, nickel, cobalt, aluminium, chromium, by ammonium nitrosophenyl-hydroxylamine—ammonium "cupferron"—as indicated on page 504. For the precipitation of copper by hypophosphites, see F. Mawrow and W. Muthmann, *Zeit. anorg. Chem.*, 11, 268, 1896; P. Wenger and N. Dürst, *Helv. Chim. Acta*, 6, 642, 1923.

[2] Remaining after the separation of the bismuth.

[3] Made by saturating aqueous ammonia with sulphur dioxide. Some use for the precipitation a mixture of 120 grms. of potassium thiocyanate and 120 grms. of sodium hydrogen sulphite dissolved in 2 litres of water (H. Tamm, *Chem. News*, 24, 91, 1874).

[4] The precipitate is practically insoluble in cold but appreciably soluble in hot water.

[5] The copper in the thiocyanate may be determined volumetrically with some advantage if the standard solutions are ready made. E. Fleischer (*Chem. News*, 19, 206, 1869) digests the precipitate in a solution of caustic alkali and washes the red precipitate of cuprous oxide with hot water until the washings give no red coloration with ferric chloride, and determines the copper by de Haen's process (page 367). S. W. Parr (*Journ. Amer. Chem. Soc.*, 22, 685, 1900; 24, 580, 1902; H. A. Guess, *ib.*, 24, 708, 1902; W. E. Garrigues, *ib.*, 19, 940, 1897; R. K. Meade, *ib.*, 20, 610, 1898; *Chem. News*, 80, 67, 1899; J. Volhard, *Liebig's Ann.*, 190, 251, 1877) dissolves the precipitated thiocyanate in 10 c.c. of a solution of potash (10 per cent.), adds 10 c.c. of ammonia (sp. gr. 0·96), and titrates with potassium permanganate until the green colour persists after warming the solution at 45°–55° for a short time. Then add more of the permanganate solution—say one-third or one-fourth of the amount already added. Let the mixture stand five minutes. Acidify the solution with 25 c.c. of dilute sulphuric acid (1 : 2), and titrate with permanganate at 60°–70° until the pink coloration appears. One gram of potassium permanganate corresponds with 0·7193 gram of cupric oxide—CuO.

[6] Cuprous thiocyanate begins to decompose if heated above 170°. A. Claus (*Journ. prakt. Chem.*, (1), 15, 401, 1838) found 3·0 per cent. of water in a sample dried at 115°; and M. Meitzendorff (*Pogg. Ann.*, 56, 63, 1842) found 1·54 per cent. when dried at 100°. Practically all the water is removed by working as described in the text. G. Fenner and J. Forschmann (*Chem. Ztg.*, 42, 205, 1918) convert the thiocyanate to oxide by ignition in a muffle at about 800° to save the time involved in drying to constant weight.

[7] I. M. Kolthoff and G. H. P. van der Meene (*Zeit. anal. Chem.*, 72, 337, 1927) recommend that, after precipitation, the solution should not be more than 0·05N with respect to thiocyanate.

cadmium, iron, cobalt, nickel and arsenic, because these elements are not precipitated under the conditions of the experiment. If antimony, tin or bismuth is present, tartaric acid should be added before precipitation.

If desired, the precipitate can be roasted to drive off the cyanogen compounds, the residue dissolved in acid and the copper determined volumetrically; or the thiocyanate can be dissolved in about 2 c.c. of concentrated nitric acid, boiled for a few minutes, treated with an excess of ammonia and the excess boiled off, treated with 2 to 3 c.c. of acetic acid, and the solution treated by de Haen's process as described below.[1] Not more than 0·0001 grm. of copper will be found in the filtrate with cadmium—if that element be present.[2]

§ 175. De Haen's Volumetric Iodine Process for Copper.

E. de Haen's process [3] is based on the fact that when an excess of potassium iodide is added to a concentrated solution of a copper salt, acidulated with acetic acid, cuprous iodide is formed, and an equivalent amount of iodine is liberated. The amount of free iodine is determined by titration with sodium thiosulphate. If the solution be too dilute, the cuprous iodide produced in the reaction just indicated re-forms the original salt. The regenerated copper salt then reacts with a further quantity of potassium iodide with liberation

[1] W. D. Brown, *Journ. Ind. Eng. Chem.*, 7, 213, 1915; G. Edgar, *Journ. Amer. Chem. Soc.*, 38, 884, 1916. G. Ineze (*Zeit. anal. Chem.*, 54, 252, 412, 1915; J. Moir, *Journ. Chem. Met. Min. Soc. S. Africa*, 18, 133, 1917; P. Fleury and P. Tavernier, *Bull. Soc. chim.*, (4), 35, 794, 1924) reduces the copper to the cuprous state by a measured excess of standard thiosulphate and, after precipitation with thiocyanate and filtration, determines the excess of thiosulphate in the filtrate. The reduction follows the course—$2CuSO_4 + 2Na_2S_2O_3 = Na_2S_4O_6 + Na_2SO_4 + Cu_2SO_4$.
[2] G. Fenner and J. Forschmann, *Chem. Ztg.*, 42, 205, 1918.
[3] E. de Haen, *Liebig's Ann.*, 91, 237, 1854; A. Rümpler, *Journ. prakt. Chem.*, (1), 105, 193, 1868; M. Flajolet, *ib.*, (2), 11, 105, 1894; D. Vitali, *Zeit. anal. Chem.*, 36, 549, 1897; L. Moser, *ib.*, 43, 597, 1904; 44, 196, 1905; E. V. Videgren, *ib.*, 48, 539, 1909; F. M. Litterscheid, *ib.*, 41, 219, 1902; *Chem. Ztg.*, 33, 263, 1909; E. Victor, *ib.*, 29, 179, 1905; F. M. Litterscheid, *ib.*, 33, 263, 1909; G. Vortmann and J. von Orlowsky, *Zeit. anal. Chem.*, 20, 416, 1881; *Monats.*, 7, 418, 1886; M. Willenz, *Rev. Chim. anal. app.*, 5, 355, 1896; *Chem. News*, 76, 243, 1897; L. Garnier, *Journ. Pharm. Chim.*, (6), 9, 326, 1899; F. Pisani, *Compt. rend.*, 47, 294, 1858; M. Haupt, *Pharm. Centr.*, 30, 509, 1889; *Chem. News*, 70, 206, 1894; L. de Bruyn and F. H. van Leert, *Rec. Trav. Chim. Pays-Bas*, 10, 119, 1891; H. Cantoni and M. Rosenstein, *Bull. Soc. chim.*, (3), 35, 1069, 1906; P. Gerlinger, *Zeit. angew. Chem.*, 19, 520, 1906; L. Moser, *Zeit. anorg. Chem.*, 56, 143, 1907; *Chem. Ztg.*, 31, 77, 1907; G. Fernekes and A. A. Koch, *Journ. Amer. Chem. Soc.*, 27, 1224, 1905; R. S. Dulin, *ib.*, 17, 346, 1895; A. H. Low, *ib.*, 18, 457, 1896; 24, 1082, 1902; *Chem. News*, 74, 52, 1896; A. M. Fairlie, *Eng. Min. Journ.*, 78, 787, 1905; A. H. Low, *ib.*, 59, 124, 1896; E. H. Miller, *ib.*, 81, 519, 1906; P. E. Browning, *Amer. J. Science*, (3), 46, 280, 1893; F. H. Heath, *ib.*, (4), 25, 513, 1908; F. A. Gooch and F. H. Heath, *ib.*, (4), 24, 65, 1907; *Chem. News*, 97, 174, 187, 1908; E. O. Brown, *Journ. Chem. Soc.*, 10, 65, 1857; J. W. Walker and M. V. Dover, *ib.*, 87, 1584, 1905; R. Williams, *Chem. News*, 58, 273, 1888; J. W. Westmoreland, *ib.*, 58, 78, 1888; *Journ. Soc. Chem. Ind.*, 5, 48, 1886; U. Tsukakoski, *Eng. Min. Journ.*, 90, 969, 1910; F. E. Lathe, *ib.*, 93, 1071, 1912; A. W. Peters, *Journ. Amer. Chem. Soc.*, 34, 422, 1912; W. C. Bray and G. M. J. MacKay, *ib.*, 32, 1193, 1910; M. E. Pozzi-Escot, *Ann. Chim. anal.*, 18, 219, 1913; E. Beck, *Chem. Ztg.*, 37, 1330, 1913; R. E. Lee, J. P. Trickey and W. H. Fegely, *Journ. Ind. Eng. Chem.*, 6, 556, 1914; R. W. Coltman, *ib.*, 7, 764, 1915; H. Ley, *Chem. Ztg.*, 41, 763, 1917; H. Koelsch, *ib.*, 37, 753, 1913; I. M. Kolthoff, *Pharm. Weekblad*, 55, 1338, 1918; P. Klason, *Svensk Kem. Tids.*, 31, 211, 1919; H. F. Bradley, *Ind. Eng. Chem.*, 12, 800, 1920; E. Lasausse, *Journ. Pharm. Chim.*, (7), 26, 401, 1922; G. Batta and G. Lathiers, *Bull. Soc. chim. Belg.*, 31, 297, 1922; N. Schoorl and H. Bergmann, *Rec. Trav. chim.*, 44, 1077, 1925; H. B. Dunnicliff and K. Ram, *Kolloid Zeit.*, 38, 168, 1926; M. I. Uschakov, *Journ. Russ. Phys. Chem. Soc.*, 60, 1151, 1928; E. H. Smith, *Chemist-Analyst*, 18, 6, 1929; 20, 10, 1931; M. Herschkovitsch, *Zeit. anorg. Chem.*, 146, 132, 1925; T. H. Whitehead and H. S. Miller, *Ind. Eng. Chem. Anal. Ed.*, 5, 15, 1933; F. Sierra, *Anales Soc. Espan. Fis. Quim.*, 31, 26, 1933; A. Wogrinz, *Chem. Ztg.*, 57, 613, 1933.

of free iodine, which produces the phenomenon of "after-blueing."[1] By increasing the concentration of potassium iodide,[2] the back reaction is retarded and the time required for the titration consequently shortened. Free mineral acids react with the potassium iodide, forming hydriodic acid. A little free acid does no particular harm but, if much acid be present, some cuprous iodide is dissolved. This acts as a catalytic agent, accelerating the oxidation of the hydriodic acid by atmospheric oxygen. This leads to "after-blueing" and to high results.

Preparation of Solution.—If the copper has been precipitated as thiocyanate (or sulphide), the precipitate is digested with, say, 5 c.c. of nitric acid (sp. gr. 1·42) until solution of the copper is complete. Evaporate the solution on a water bath with hydrochloric acid in order to expel completely all red fumes of nitrogen oxides. This point is very important since nitrous acid is produced by the solution of the copper in the nitric acid. Unless the nitrous acid is entirely removed,[3] it will react with the potassium iodide with liberation of iodine:

$$2HI + 2HNO_2 = 2H_2O + 2NO + I_2$$

Redissolve the residue in 25 c.c. of water and neutralise the acid by the addition of a few drops of ammonia.[4] Boil the solution to expel the ammonia. Add 2 c.c. of concentrated acetic acid in order that the acid may be in slight excess.[5] If necessary, boil to ensure the complete dissolution of the copper. Cool. The cold solution should occupy about 50 c.c. If less, make the solution up to this volume with water.[6]

The Titration.—Dissolve 3 grms. of potassium iodide in the solution.[7]

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[1] When the blue colour of the "starch iodide" has been removed by the sodium thiosulphate, and more iodine passes into solution, the blue "starch iodide" colour will again appear. If this blue reappears after the colour has once been discharged by the titration, the phenomenon is called "after-blueing"—J. H. Davies and E. P. Perman, *Chem. News*, 93, 225, 1906; K. Sugiura and P. A. Kober, *Journ. Amer. Chem. Soc.*, 34, 818, 1912; E. R. E. Muller, *Chem. Ztg.*, 38, 1137, 1914; H. Dubovitz, *ib.*, 39, 585, 1915.

[2] P. A. Shaffer and A. F. Hartmann (*Journ. Biol. Chem.*, 45, 349, 1921) consider that the final concentration of potassium iodide should be about 0·25 M to prevent reversal of the reaction.

[3] A. H. Low (*l.c.*) oxidises the nitrous acid by boiling the solution with 5 c.c. of bromine water until the bromine is expelled. E. C. Kendall (*Journ. Amer. Chem. Soc.*, 33, 1947, 1911) boils with sodium hypochlorite and afterwards destroys the excess of hypochlorite with phenol. M. E. Pozzi-Escot (*l.c.*), H. Koelsch (*l.c.*) and R. Intonti (*Ann. Chim. appl.*, 20, 583, 1930) remove the nitrous acid by the addition of urea.

[4] Or sodium bicarbonate, not the carbonate (page 291). Note that iodine may be carried off if much carbon dioxide escapes from the solution after the addition of the potassium iodide.

[5] The solution should not contain more than 3 c.c. of nitric, hydrochloric or sulphuric acid, or 25 c.c. of 50 per cent. acetic acid, per 100 c.c. of solution. For the action of hydrochloric acid on sodium thiosulphate titrations, see J. T. Norton, *Amer. J. Science*, (4), 7, 287, 1899; *Chem. News*, 80, 27, 1899. S. U. Pickering (*Journ. Chem. Soc.*, 37, 135, 1880) showed that more iodine is required to oxidise the thiosulphate as the proportion of hydrochloric acid increases.

[6] C. E. Smith, *Met. Chem. Eng.*, 14, 379, 1916.

[7] Or add about 6 c.c. of a 50 per cent. solution of potassium iodide. An excess of potassium iodide does no harm; too little will make the subsequent titration tedious owing to the gradual solution of precipitated iodine. An excess is therefore necessary to keep the precipitated iodine in solution; indeed, E. H. Smith (*l.c.*) says that the end-point is sharper if sufficient potassium iodide be added to dissolve the precipitated cuprous iodide. A "super-excess" means waste, and potassium iodide is expensive. G. Bruhns (*Chem. Ztg.*, 42, 301, 1918; *Zeit. anal. Chem.*, 59, 337, 1920; P. Fleury and L. Boutot, *Bull. Soc. chim. biol.*, 4, 361, 1922; P. Fleury, *Bull. Soc. chim.*, (4), 35, 230, 1924; W. Orlik and W. Tietze, *Chem. Ztg.*, 54, 174, 1930; I. M. Kolthoff, *ib.*, 42, 609, 1918) adds but a little potassium iodide to the copper solution and titrates with a mixture of thiosulphate and potassium thiocyanate. The latter reacts with the cuprous iodide first formed, to give the equivalent amount of potassium

Nearly white cuprous iodide separates and iodine is liberated. Shake the solution vigorously. The reaction is represented by the equation:

$$2CuCl_2 + 4KI \rightleftharpoons Cu_2I_2 + I_2 + 4KCl$$

The free iodine which separates colours the solution brown. The solution should be cold and kept cold to prevent loss of iodine. To avoid oxidation titrate the solution *at once* with a standard solution of sodium thiosulphate [1] until the brown colour of the iodine has changed to a faint straw yellow.[2] Then add 5 c.c. of a cold solution of starch (page 285) in order to develop the "iodine blue," and continue the titration cautiously, drop by drop, until the iodine blue is discharged. A drop in excess will suffice. The action of the thiosulphate on the iodine is represented by the equation:

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$$

The blue colour of the "starch iodide" returns on exposure to the atmosphere. If the solution remains colourless two minutes, the titration may be considered finished.[3]

If 1 c.c. of the standard solution of sodium thiosulphate represents 0·0159 grm. of copper oxide, and 25 c.c. of the sodium thiosulphate solution be required for the titration, then the solution under investigation contained the equivalent of $25 \times 0·0159 = 0·3975$ grm. of copper oxide.

Influence of Foreign Substances.—If the blue colour of the "starch iodide" returns almost immediately after a titration, and this again after the addition of two more drops of thiosulphate, the titration will probably be unreliable owing to the failure to destroy the nitrous acid present in the solution at an earlier stage of the operation. Excessive dilution, excessive amounts of acetic acid and the presence of sodium or ammonium acetate retard the reaction between the copper salt and the potassium iodide. This leads to low results. Hence the care recommended above to remove the ammonia. In the presence of these retarding agents, the titration is somewhat tedious, since

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iodide, thus decreasing the quantity of potassium iodide initially needed. This modification does not give reliable results (see D. Krüger and E. Tschirch, *Zeit. anal. Chem.*, **97**, 161, 1934), but H. W. Foote and J. E. Vance (*Journ. Amer. Chem. Soc.*, **57**, 845, 1935) have found that if a little of a soluble thiocyanate be added towards the end-point of the usual iodine titration results are obtained comparable with the best volumetric methods. See also J. Bitskei, *Zeit. anal. Chem.*, **102**, 35, 1935.

[1] STANDARD SOLUTION OF SODIUM THIOSULPHATE.—Dissolve 12 grms. of the pure anhydrous salt in a litre of pure, recently boiled distilled water. If the hydrated salt is used, take 19 grms. The latter is first reduced to powder and dried between sheets of blotting-paper. After the solution has stood about a fortnight, it is standardised by weighing 0·10, 0·15 and 0·20 grm. of pure electrolytic copper foil separately in three 250 c.c. Erlenmeyer flasks. Warm the copper with 5 to 10 c.c. of nitric acid (sp. gr. 1·20). Make the volume of the solution in each flask up to about 25 c.c., and evaporate on a steam bath in order to expel red fumes of nitrogen oxides. Then treat each solution as indicated in the text. W. C. Grant, *Chemist-Analyst*, **13**, 21, 1915. For the stabilisation and standardisation of thiosulphate solutions for this process, see A. H. Low, *Chemist-Analyst*, **30**, 18, 1920; L. O. Hill, *Ind. Eng. Chem. Anal. Ed.*, **8**, 200, 1936.

[2] If the end-point does not appear before 25 c.c. of the thiosulphate have been added, add 2 grms. more potassium iodide. At this stage J. R. Caldwell (*Journ. Amer. Chem. Soc.*, **57**, 96, 1935) recommends the addition of 0·5 to 1 c.c. of a 4 per cent. alcoholic solution of white shellac, drop by drop. The liquid is stood for 30 seconds before completing the titration. The addition of the shellac prevents the blue starch-iodide complex being carried down by the precipitated cuprous iodide and the end-point is said to be much sharper.

[3] RECOVERY OF IODINE.—For the recovery of iodine from cuprous iodide, see F. T. van Voorst, *Chem. Weekblad*, **28**, 129, 440, 1931; J. J. Hansma, *ib.*, **28**, 183, 1931. For the recovery of iodine from the aqueous residues, see footnote 3, page 289.

the "after-blueing" has to be followed up for a long time. The presence of a large amount of alkali salts – particularly sulphates and nitrates—leads to wrong results.

Ferric acetate liberates iodine from potassium iodide; ferric phosphate does not. Hence, if a little iron be present, some recommend the addition of sodium phosphate.[1] If much iron be present, the copper should first be separated as sulphide, metal or thiocyanate. Bismuth forms a brown-coloured iodide which is very like the colour of the iodine in solution and it also imparts a dirty green colour to the starch indicator, so that the change is not from blue to colourless, but from dirty green to yellowish-white. Hence, while bismuth does not actually interfere, its presence obscures the end-point and too much thiosulphate may be run in before the starch is added. Lead, arsenic and antimony interfere [2] with the determination and should be removed before titrating.[3] Lead may be removed as sulphate, bismuth as phosphate, or both as peroxides by hydrogen peroxide in alkaline solution (page 362).

Errors.—The chief points requiring attention are:--(1) Errors due to the use of insufficient potassium iodide; (2) too much acid liberates iodine from potassium iodide in presence of air, but sufficient acid must be present to give a prompt liberation of iodine and a sharp end-point during the titration—sulphuric and acetic acids can be used; nitric and hydrochloric acids are not so good; (3) loss of iodine by volatilisation (page 302); (4) the solution to be determined should occupy as small a volume as possible and be titrated with as dilute a solution of thiosulphate as is consistent with a good end-point; and (5) the end-point is modified in the presence of a large excess of cuprous iodide. The mixture of starch and cuprous iodide, just before the end-point is reached, assumes a chocolate-brown coloration, and this changes to a pale buff colour with the last necessary drop of thiosulphate. The end-point has occurred when another drop of thiosulphate does not diminish the prevailing light tint of the mixture. So long as a drop of thiosulphate falling on the quiet surface of the liquid under titration produces a perceptible white area, the end-point has not been reached.

§ 176. The Evaluation of Copper Oxide and Carbonate.

Dissolution of the Copper Oxide.—Digest, say, 0·5 grm. of the oxide or carbonate on a hot plate with sulphuric acid or with 6 to 10 c.c. of nitric acid (sp. gr. 1·4) and 7 c.c. of sulphuric acid (sp. gr. 1·84). Heat the solution until the excess of sulphuric acid has been nearly expelled. Calcined copper oxide dissolves rather slowly, while copper oxide which has not been calcined at a

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[1] L. Moser (*Zeit. anal. Chem.*, **43**, 597, 1904) adds an excess of sodium pyrophosphate —$Na_4P_2O_7$—to determine copper in the presence of arsenic and iron by the iodine process. Complex phosphates are formed; of these, the copper salt is alone decomposed by acetic acid. H. Ley, *Chem. Ztg.*, **41**, 763, 1917; I. M. Kolthoff, *ib.*, **42**, 609, 1918; I. W. Wark, *Journ. Chem. Soc.*, **121**, 358, 1922; F. L. Hahn and H. Windisch, *Ber.*, **56B**, 598, 1923, all recommend the use of phosphates. Anon. (*Journ. Soc. Chem. Ind.*, **34**, 462, 1915; H. F. Bradley, *Chemist-Analyst*, **17**, 14, 1928; B. Park, *Ind. Eng. Chem. Anal. Ed.*, **3**, 77, 1931) uses alkali fluoride to suppress the iron, while A. Wober (*Zeit. angew. Chem.*, **35**, 336, 1922) precipitates the iron as ferric hydroxide by blowing air through the ammoniacal solution at 70°. For the simultaneous determination of copper and iron, see H. Ley (*l.c.*) and I. W. Wark (*l.c.*).

[2] According to Fernekes and Koch (footnote 4, page 365), cadmium, zinc, aluminium, arsenic, antimonic and stannic salts do not interfere. For the determination of arsenic and copper in mixed solution, see I. M. Kolthoff and C. J. Cremer, *Pharm. Weekblad*, **58**, 1620, 1921.

[3] C. and J. J. Beringer, *A Textbook of Assaying*, London, 201, 1908.

high temperature dissolves quickly.   When cold, add 25 c.c. of water [1] and, if necessary, filter.

Precipitation of the Copper.—Place two strips of metallic aluminium [2]—say 15 cm. by 2·5 cm. by 1 mm.—in the solution so that one end of each strip rests against the side of the beaker.   Cover the beaker with a clock-glass to prevent loss by spurting [3] and heat the solution to boiling.   Metallic copper is precipitated.   When all the copper is precipitated—about a quarter of an hour—decant the liquid through a 9 cm. filter-paper.   Wash the copper [4] on the aluminium plates and on the filter-paper with a weak solution of hydrogen sulphide in air-free water to prevent oxidation of the copper.   Reject the filtrate and washings.[5]

Dissolution of the Copper.—Dissolve the copper from the aluminium plates in a slight excess of nitric acid (sp. gr. 1·3) and remove the plates from the beaker.   Pour the solution through the filter-paper and collect the filtrate in a second beaker.   Wash the first beaker and the filter-paper and then treat the solution as described under de Haen's process (page 367), care being taken to expel nitrous acid from the solution.

Errors.—The Committee of the American Chemical Society, "On Uniformity in Technical Analysis," [6] reported in 1904 that the following numbers represent the extremes sent in by nineteen analysts for a sample of cupriferous slag:—

	SiO_2.	Fe.	Al_2O_3.	CaO.	MgO.	Zn.	Mn.	Cu.	S.
Highest	35·15	32·20	7·16	13·53	3·21	4·25	1·53	0·46	1·98
Lowest	31·27	30·33	3·24	10·73	1·00	1·87	0·11	0·20	1·45

The remarks made on the analyses of the argillaceous limestone, on page 245, are applicable here.[7]

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[1] Copper is slightly soluble in concentrated sulphuric and hydrochloric acids; hence the acidity of the solution should be feeble.

[2] The precipitation by aluminium is quantitative when acids, other than sulphuric acid, are absent.   D. Tommasi, *Bull. Soc. chim.*, (2), **37**, 443, 1882; *ib.*, (3), **17**, 440, 1897; *Chem. News*, **46**, 62, 1882; A. H. Low, *Journ. Amer. Chem. Soc.*, **18**, 458, 1896; G. E. Perkins, *ib.*, **24**, 478, 1902; *Chem. News*, **86**, 86, 1902; E. V. Videgren, *Zeit. anal. Chem.*, **48**, 539, 1909; E. E. Kern and M. H. Morris, *School Mines Quart.*, **35**, 1, 1914; J. B. Senderens, *Bull. Soc. chim.*, (3), **15**, 208, 1896.   For magnesium: A. Villiers and F. Borg, *Compt. rend.*, **116**, 1524, 1893; E. G. Bryant, *Chem. News*, **76**, 30, 1897; S. A. Sworn, *ib.*, **76**, 59, 1897.   See also page 309.   For zinc: G. H. Pfaff, *Handbuch der analytischen Chemie*, Altona, 269, 1822; F. Mohr, *Zeit. anal. Chem.*, **1**, 143, 1862; C. Ullgren, *ib.*, **7**, 442, 1868; F. Field, *Chem. News*, **1**, 62, 73, 1860.   For cadmium: A. Classen, *Journ. prakt. Chem.*, (1), **96**, 259, 1865.   For iron: A. A. Julien, *Chem. News*, **24**, 9, 1871 (page 170).   The iron should dissolve uniformly without the separation of black particles and the formation of ridges on the surface.

[3] Cadmium used in place of aluminium does not spurt so much.

[4] The copper film has its own characteristic red colour.   If the solution contained any arsenic or antimony, the copper will be contaminated and appear dirty brown.

[5] At this stage Field washed, dried and weighed the metallic copper.   He found that the copper precipitated by either zinc or iron always contained traces of these metals; at the same time, a small amount of copper in the primary solution always escapes precipitation.   In commercial analyses, Field considers that the small amount of foreign metal precipitated with the copper compensates for that left in the primary solution.

[6] *Journ. Amer. Chem. Soc.*, **26**, 1644, 1904.

[7] For the simultaneous determination of copper, cuprous and cupric oxides in admixture, see D. Nishida and K. Hirabayashi, *Journ. Chem. Ind. Japan*, **26**, 1123, 1923; S. Zerfoss and M. L. Willard, *Ind. Eng. Chem. Anal. Ed.*, 8, 303, 1936; and for copper-cuprous oxide mixtures, W. D. Bonner and B. D. Kaura, *Ind. Eng. Chem.*, **19**, 1288, 1927; L. C. Hurd and A. R. Clark, *ib.*, *Anal. Ed.*, 8, 380, 1936.

§ 177. The Colorimetric Determination of Copper— Carnelly's Ferrocyanide Process.

In cases where but small quantities of copper are likely to be present, in red lead, for example, the copper is usually determined colorimetrically,[1] from the intensity of the colour of ammoniacal,[2] ferrocyanide,[3] bromide [4] or chloride [5] solutions.

Potassium ferrocyanide, in acid solutions of copper, produces an earthy brown coloration which can be detected when 1 part of copper is present in 1,000,000 parts of solution. In neutral solutions, 1 part of copper can be detected in 1,500,000 parts of solution; and in neutral solutions containing ammonium nitrate, 1 part of copper can be detected in 2,500,000 parts of solution.[6] Hence the ferrocyanide test is made with neutral solutions in the presence of ammonium nitrate. The sensitivity is similarly increased if ammonium chloride be substituted for the nitrate.

The Standard Solution.—Pipette 1 c.c. of an aqueous solution of potassium ferrocyanide [7] into a 100 c.c. flask; add 5 c.c. of an aqueous solution of

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[1] A. E. von Hubert, *Berg. Hütt. Ztg.*, 8, 667, 1849; 10, 804, 1851; V. Eggertz, *ib.*, 21, 218, 1862; *Zeit. anal. Chem.*, 2, 434, 1863; F. Dehms, *ib.*, 3, 218, 1864; *Dingler's Journ.*, 172, 160, 1864; G. Panten, *ib.*, 170, 391, 1863; C. Stammer, *ib.*, 159, 641, 1861; A. Payen, *ib.*, 27, 372, 1828; V. A. Jacquelain, *Journ. prakt. Chem.*, (1), 46, 174, 1849; A. Müller, *ib.*, (1), 60, 474, 1853; *Zeit. anal. Chem.*, 2, 434, 1863; M. Bergeron and L. l'Hôte, *Compt. rend.*, 80, 268, 1875; J. Wagmeister, *Oester. Zeit. Berg. Hütt.*, 13, 270, 1865; J. Parry and J. J. Morgan, *Chem. News*, 67, 259, 1893; T. P. Blunt, *ib.*, 32, 3, 1875; 33, 7, 1876; M. M. P. Muir, *ib.*, 33, 11, 1876; M. W. Iles, *ib.*, 34, 16, 1876; M. Lucas, *Bull. Soc. chim.*, (3), 19, 815, 1898; *Chem. News*, 79, 67, 1899; G. L. Heath, *Journ. Amer. Chem. Soc.*, 19, 24, 1897; J. D. A. Smith, *Trans. Amer. Inst. Min. Eng.*, 30, 851, 1900; L. W. Winkler, *Zeit. angew. Chem.*, 26, 38, 1913; E. R. Budden and H. Hardy, *Analyst*, 19, 169, 1894; S. G. Clarke and B. Jones, *ib.*, 54, 333, 1929; C. Pyriki, *Zeit. anal. Chem.*, 64, 325, 1924; A. B. Shakhkeldian, *Journ. Appl. Chem. Russia*, 2, 475, 1929; R. Biazzo, *Ann. Chim. appl.*, 16, 96, 1926; D. L. Drabkin and C. S. Waggoner, *Journ. Biol. Chem.*, 89, 51, 1930.

[2] G. Bischof, *Dingler's Journ.*, 184, 433, 1867; J. Milbauer and V. Stanek, *Zeit. anal. Chem.*, 46, 644, 1907; A. Austin, *Min. Eng. World*, 33, 753, 1910; B. S. White, *Ind. Eng. Chem.*, 7, 1035, 1915; I. F. Ilchenko and K. M. Stakhorskyi, *Ukrain. Khem. Zhur.*, 3, 237, 1928. According to A. Jaworowsky (*L'Orosi*, 19, 195, 1896), the colour reaction is much more sensitive if a drop or two of phenol be added to the ammonia.

[3] T. Carnelly, *Chem. News*, 32, 308, 1875; W. B. Pritz, A. Guillaudeu and J. R. Withrow, *Journ. Amer. Chem. Soc.*, 35, 168, 1913; *Chem. News*, 109, 134, 1914; L. W. Winkler, *Zeit. angew. Chem.*, 27, 544, 1914; R. F. Heath, *Min. Scientific Press*, 114, 624, 1917. Compare L. A. McDowell and H. L. Johnston, *Journ. Amer. Chem. Soc.*, 58, 2010, 1936.

[4] G. Denigès and E. Simonot, *Journ. Pharm. Chim.*, (7), 11, 186, 1915.

[5] N. V. Mandrika, *Zhur. Prikladnoi Khem.*, 2, 317, 1929.

[6] This is nearly the same delicacy as hydrogen sulphide, which gives a brown coloration with copper solutions when 1 part of copper is present in 2,500,000 parts of solution—A. Wagner, *Zeit. anal. Chem.*, 20, 349, 1881; A. Castiglioni, *Zeit. anal. Chem.*, 97, 270, 1934. The ammonia test is one-tenth as sensitive as the ferrocyanide test.—A. J. Cooper, *Journ. Soc. Chem. Ind.*, 5, 84, 1886. The hydrogen sulphide reaction is not recommended for the colorimetric test because of the disturbing effects of lead. For the colorimetric determination of copper by sodium diethyldithiocarbamate, see T. Callan and J. A. R. Henderson, *Analyst*, 54, 650, 1929; L. A. Haddock and N. Evers, *ib.*, 57, 495, 1932; R. W. Thatcher, *Journ. Amer. Chem. Soc.*, 55, 4524, 1933; W. D. McFarlane, *Biochem. J.*, 26, 1022, 1932; W. R. G. Atkins, *Journ. Marine Biol. Assoc. U.K.*, 19, 63, 1933; H. W. Moseley, A. G. Rohwer and M. C. Moore, *Science*, 79, 507, 1934; L. W. Conn, A. H. Johnson, H. A. Trebler and V. Karpenko, *Ind. Eng. Chem. Anal. Ed.*, 7, 15, 1935; E. Laget, *Ann. Chim. anal. Chim. appl.*, 17, 145, 1935. For the determination of copper (also zinc and lead) in silicate rocks by diphenylthiocarbazone, see E. B. Sandell, *Ind. Eng. Chem. Anal. Ed.*, 9, 464, 1937; E. Stolze, *Bodenk. Pflanzenernähr.*, 1, 115, 1936.

[7] POTASSIUM FERROCYANIDE SOLUTION.—Dissolve 1 grm. of potassium ferrocyanide in 25 c.c. of water.

ammonium nitrate,[1] and make the solution up to 100 c.c. with distilled water. Transfer this solution, or an aliquot portion, to the right test glass of the colorimeter.

The Test Solution.—The solution under investigation must be neutralised.[2] If free potash be present, it is first neutralised by a slight excess of acid, then a slight excess of ammonia is added. Boil off the excess of ammonia until the solution is neutral. If the solution is acid, add a slight excess of ammonia and boil off the excess until the solution is neutral. Make the cold solution up to a definite volume, say 100 c.c. Pipette 1 c.c. of the solution of potassium ferrocyanide into a 100 c.c. flask; add 5 c.c. of the ammonium nitrate solution and then add an aliquot portion, say 50 c.c., of the solution under investigation. Make the solution up to the mark with water. Transfer the whole solution, or an aliquot portion, to the left test glass of the colorimeter.

The Comparison.—Fill a burette with a standard solution of copper sulphate.[3] The burette may read to, say, $\frac{1}{50}$th c.c. Run the copper sulphate solution gradually from the burette into the right test glass of the colorimeter, with constant stirring, until the tints of the test solution and the standard solution are the same.

Calculations.—A gram of red lead gave a solution which was made up to 100 c.c. 100 c.c. of the standard solution needed 0·78 c.c. of a standard copper solution to produce uniformity of tint. The 0·78 c.c. of the standard copper solution contained 0·000078 grm. of copper oxide. Hence 100·78 c.c. of the standard contained the same amount of copper oxide as the 100 c.c. of the given sample. Thus the sample contained 0·0078 per cent. of copper oxide.

Accuracy of the Results.—The following results illustrate the accuracy of the process with solutions containing known quantities of copper oxide:—

CuO used	.	100	10	1·15	0·9	0·8	0·7	0·5	mgrm.
CuO found	.	102·01	11·2	1·19	0·91	0·82	0·71	0·52	mgrm.

The amount of copper oxide so determined is rather too high with the more concentrated solutions, but the results are quite good with small quantities.

Influence of Foreign Substances.—With moderate proportions an excess of the ferrocyanide solution does not affect the accuracy of the method. Similar remarks apply to the ammonium nitrate. For example, no difference could be detected by Carnelly in the results obtained with solutions containing 5 and 15 c.c. of the respective salt solutions. Ammonium chloride, sodium chloride, calcium chloride, calcium sulphate, magnesium sulphate and sugar did not appear to affect the results. It is, however, best to destroy the organic matter, if present, by evaporation with nitric acid.

Influence of Lead.—Lead salts form a white precipitate with potassium ferrocyanide which does not interfere with a comparison of the colours. Carnelly made up a solution containing 2 grms. of lead nitrate (1·25 grms. Pb) with 0·255 grm. of copper nitrate in a litre of water. Varying proportions of this solution were taken, with the following results:—

Cu used	.	.	0·77	0·70	0·49	0·51	0·35	mgrm.
Cu found	.	.	0·80	0·75	0·51	0·49	0·38	mgrm.

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[1] AMMONIUM NITRATE SOLUTION.—Dissolve 100 grms. of the salt in a litre of water.

[2] Free acids make the tint paler, free ammonia dissolves the precipitate produced by the ferrocyanide and free potash decomposes it.

[3] STANDARD SOLUTION OF COPPER SULPHATE.—Dissolve 0·3138 grm. of pure copper sulphate—$CuSO_4.5H_2O$—in a litre of water. One c.c. of the solution contains 0·0001 grm. of CuO.

Hence relatively large amounts of lead have no appreciable effect on the accuracy of the comparison.

Influence of Iron.—If iron be present, the solution is oxidised with a few drops of nitric acid and evaporated to a small bulk. Precipitate the iron with ammonia, filter and wash. Dissolve the precipitate in nitric acid and reprecipitate with ammonia. Filter and wash. Mix the filtrates and boil the solution to drive off the ammonia. The following represent the results obtained with varying amounts of iron,[1] which were separated before the copper was determined:—

Fe used	.	.	.	0	0·20	2·40	3·00 mgrm.
Cu used	.	.	.	0·66	0·51	0·61	0·76 mgrm.
Cu found	.	.	.	0·66	0·53	0·69	0·79 mgrm.

The results are therefore quite satisfactory.[2]

§ 178. The Determination of Copper with α-Benzoin Oxime ("Cupron").

The use of certain organic precipitants enables copper to be determined gravimetrically when the amount of metal present is so small that otherwise a colorimetric method would have to be adopted. Of these reagents probably α-benzoin oxime is the best known and most satisfactory.[3]

Dilute ammonia solution is added in liberal excess to the neutral solution of copper,[4] containing little, if any, ammonium salts. The solution is heated to boiling and a 4 per cent. alcoholic solution [5] of α-benzoin oxime added dropwise until the blue copper colour disappears. The solution is then filtered through a weighed Gooch crucible, or a sintered glass filter crucible, dried at 110°. The green precipitate is washed first with a hot 1 per cent. solution of ammonia until free from mineral salts, and then with hot alcohol to remove excess of the precipitant, if any. After drying at 110°, the precipitate is weighed as $C_{14}H_{11}O_2NCu$, with 22·02 per cent. of copper.[6]

§ 179. The Gravimetric Determination of Cadmium as Sulphate.

Precipitation as Cadmium Sulphide.—When hydrogen sulphide is passed through a solution containing more than 0·25 grm. of crystalline cadmium sulphate in 100 c.c. of water, cadmium sulphide separates as a canary yellow curdy precipitate which quickly settles, leaving the supernatant liquid yellow and opaque. If the mixture be heated to boiling, the precipitate becomes

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[1] Small amounts of iron are determined by the thiocyanate process (page 185).

[2] M. Frommes (*Zeit. anal. Chem.*, **97**, 36, 1934) reviews some of the more recent work on the determination of copper.

[3] F. Feigl, *Ber.*, **56B**, 2083, 1923; F. Feigl, G. Sicher and O. Singer, *ib.*, **58B**, 2294, 1925; R. Strebinger, *Mikrochem.*, **1**, 72, 1923; E. Azzalin, *Ann. Chim. appl.*, **15**, 373, 1925; H. A. Kar, *Ind. Eng. Chem. Anal. Ed.*, **7**, 193, 1935; Z. Gruzewska and G. Roussel, *Compt. rend. Soc. biol.*, **121**, 289, 1936.

[4] The solution should contain not more than about 0·05 grm. of copper.

[5] The amount of benzoin oxime used should be about four times the weight of copper present.

[6] For the determination of copper with 8-hydroxyquinoline, see R. Berg, *Zeit. anal. Chem.*, **70**, 341, 1927; J. Calvet, *Compt. rend.*, **195**, 148, 1932; with 5 : 7-dibromo-8-hydroxyquinoline, L. W. Haase, *Zeit. anal. Chem.*, **78**, 113, 1929; with salicylaldoxime, F. Ephraim, *Ber.*, **63B**, 1928, 1930; *ib.*, **64B**, 1210, 1215, 1931; W. Reif, *Zeit. anal. Chem.*, **88**, 33, 1932; S. Astin and H. L. Riley, *Journ. Chem. Soc.*, 314, 1933; H. L. Riley, *ib.*, 895, 1933; E. Azzarello and A. Accardo, *Ann. Chim. appl.*, **23**, 483, 1933; M. Ishibashi and H. Kishi, *Journ. Chem. Soc. Japan*, **55**, 1060, 1067, 1934; F. Alten, B. Wandrowsky and E. Knippenberg, *Mikrochem.*, **20**, 74, 1936; M. Chambers, *Chemist-Analyst*, **26**, 52, 1937; I. Ubaldini, *Chim. e Ind.* (Italy), **19**, 65, 1937; J. Mironoff, *Bull. Soc. chim. Belg.*, **45**, 1, 1936.

orange-yellow [1] and the supernatant liquid is left almost clear and colourless. With solutions containing about 0·01 grm. of the sulphate, there is no precipitate and the solution is distinctly yellow. On standing for 24 hours, however, the colloidal sulphide, to which the colour of the liquid is due, coagulates and precipitates. Hydrochloric acid has a solvent action on the sulphide. Thus Meldrum found that for w grm. of crystalline cadmium sulphate per 10 c.c. of water, v c.c. of concentrated hydrochloric acid were required to dissolve the resulting sulphide, the corresponding values of w and v being indicated below:—

w.			0·050	0·040	0·030	0·020	0·010	0·005	0·0025	grm.
v at 10°		.	3·0	3·5	3·0	2·5	2·0	1·5	1·5	c.c.
v at 100°		.	1·0	0·8	0·8	0·8	0·5	0·4	0·3	c.c.

Hence the failure to precipitate all the cadmium sulphide may be due to the presence of an excess of hydrochloric acid or to the liberation of this acid when chlorides are decomposed by hydrogen sulphide [2]:—$MCl_2 + H_2S = MS + 2HCl$. If 100 c.c. of the solution contain not more than the equivalent of 14 c.c. of hydrochloric acid (sp. gr. 1·12), the separation of cadmium sulphide will be complete in the cold, but if over 20 c.c. of this acid be present no precipitate will be formed in cold solution. At 70°, 5 c.c. of an acid of sp. gr. 1·01 is the limit for complete precipitation and 19 c.c. of this acid, per 100 c.c. of solution, completely inhibits precipitation at this temperature.[3] Consequently the adjustment of the acidity of the solution needs careful attention. Sulphuric and acetic acids have a much smaller solvent action. The separation of cadmium sulphide is complete in dilute sulphuric acid (sp. gr. 1·19) in the *cold*. If but 5–40 c.c. of this acid be present in 100 c.c. of solution, the precipitate is finely divided and difficult to filter; with 40–70 c.c., the precipitate is more compact and easier to filter; and with 70–100 c.c. of this acid in 100 c.c. of solution the precipitation is complete, but the gas must be conducted through the solution a long time. In *hot* solutions (70°), if over 30 c.c. of this acid be present, traces of cadmium will remain in solution. The optimum acidity is given variously as from 3 to 13 c.c. of concentrated sulphuric acid per 100 c.c.[4] but about 7 to 8 c.c. is the most favoured value.

If any cadmium should be present, it will be found in the slightly acid filtrate from the copper thiocyanate. Accordingly, adjust the acidity of the solution so that it contains from 7 to 8 c.c. of free sulphuric acid per 100 c.c., heat to about 70° and pass hydrogen sulphide through it until cold; cadmium sulphide, more or less contaminated with double salts,[5] will be precipitated.[6]

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[1] The colour of the precipitate is determined by the nature of the mother liquid, temperature, etc. The colour of the cadmium sulphide may vary from light yellow to an orange-brown. N. von Knobukow, *Journ. prakt. Chem.*, (2), **39**, 412, 1889; G. Büchner, *Chem. Ztg.*, **11**, 1087, 1107, 1887.

[2] For the equilibrium $CdCl_2 + H_2S \rightleftharpoons CdS + 2HCl$, see W. Manchot, G. Grassl and A. Schreeberger, *Zeit. anal. Chem.*, **67**, 177, 1925.

[3] O. Follenius, *Zeit. anal. Chem.*, **13**, 411, 1874.

[4] O. Follenius, *Zeit. anal. Chem.*, **13**, 411, 1874; R. Meldrum, *Chem. News*, **79**, 170, 1899; E. T. Allen and J. L. Crenshaw, *Zeit. anorg. Chem.*, **79**, 125, 1913; W. D. Treadwell and K. S. Guiterman, *Zeit. anal. Chem.*, **52**, 459, 1913; W. Cooper, *Chem. News*, **110**, 250, 1914; E. Schramm, *Journ. Ind. Eng. Chem.*, **11**, 110, 1919; L. W. Winkler, *Zeit. angew. Chem.*, **34**, 383, 1921; G. Luff, *Zeit. anal. Chem.*, **65**, 97, 1924; J. G. Fairchild, *Chemist-Analyst*, **20**, 5, 1931; W. N. Stull, *Journ. Amer. Chem. Soc.*, **23**, 508, 1901.

[5] *E.g.* $CdS.CdCl_2$; $CdS.CdSO_4$—O. Follenius, *Zeit. anal. Chem.*, **13**, 411, 1874.

[6] If zinc is present, the sulphide precipitated from 4 to $5N$-H_2SO_4 solution should be redissolved in dilute hydrochloric acid (1 : 1) and reprecipitated with hydrogen sulphide— W. D. Treadwell and K. S. Guiterman (*l.c.*). According to G. Luff (*l.c.*), a cleaner separation of cadmium from zinc is effected if ammonium sulphate be present in the solution. See also K. Chalupny and K. Breisch, *Chem. Ztg.*, **48**, 349, 1924.

Conversion of the Sulphide to Sulphate.—The sulphide is filtered; washed with water containing about 5 per cent. of ammonium nitrate; dissolved in hot hydrochloric acid (1 : 3); and heated on a water bath with a slight excess of sulphuric acid. The solution is then evaporated to dryness in a weighed platinum crucible supported over a ring burner, so that there may be no loss by spurting. The crucible is then placed in a larger crucible, and heated to redness [1] until no more white fumes of sulphuric acid are evolved. Cool in a desiccator. If the sulphate is tinged with a yellow colour, some oxide is present. In that case, add a drop of sulphuric acid to moisten the mass and again ignite. Cool in a desiccator and weigh as cadmium sulphate— $CdSO_4$. The cadmium sulphate so obtained should be white in colour and dissolve to a perfectly clear solution in water. Every gram of cadmium sulphate—$CdSO_4$—corresponds with 0·6159 gram of cadmium oxide—CdO. The results are excellent.[2] For instance, Follenius found with solutions containing 0·4036 grm. of cadmium sulphate:

$CdSO_4$ found	.	0·4036	0·4036	0·4033	0·4038 grm.
Error	. .	0	0	− 0·0003	+ 0·0002 grm.

§ 180. The Volumetric Determination of Cadmium—Berg's Process.

The cadmium may be determined volumetrically, instead of gravimetrically as sulphate, when a standard solution of iodine is available.[3] Collect the precipitated cadmium sulphide on a filter-paper or in a Gooch crucible packed with asbestos. Wash the precipitated sulphide with air-free water and transfer it by washing with 250 c.c. of air-free water to a 500-c.c. Erlenmeyer's flask. An excess of iodine solution [4] is added along with 10 c.c. of hydrochloric acid (sp. gr. 1·19). The reaction which occurs is represented by the equation:

$$CdS + 2HCl + I_2 = CdCl_2 + 2HI + S$$

[1] On evaporating a solution of cadmium sulphate with sulphuric acid, crystals of $CdSO_4.H_2O$ are formed (B. Kühn, *Arch. Pharm.*, (2), **50**, 286, 1847; *Schweigger's Journ.*, **60**, 344, 1830; K. von Hauer, *Journ. prakt. Chem.*, (1), **64**, 477, 1855; (1), **72**, 372, 1857; G. Wyrouboff, *Bull. Soc. Min.*, **11**, 275, 1888; **12**, 366, 1889; F. Mylius and R. Funk, *Ber.*, **30**, 832, 1897; *Zeit. anorg. Chem.*, **13**, 157, 1897; M. de Schulten, *Compt. rend.*, **107**, 405, 1888). At 100° the water of crystallisation is given off and anhydrous cadmium sulphate is obtained. Cadmium sulphate can be heated for a long time at a red heat, under the conditions described in the text, without decomposition. At a still higher temperature, the sulphate begins to decompose, first acquiring a yellow tint and finally passing to a dark brown-coloured oxide. If ammonium chloride be present, ammonium sulphate and cadmium chloride may be formed.

[2] H. Rose, *Ausführliches Handbuch der analytischen Chemie*, Braunschweig, **2**, 149, 1871; O. Follenius, *Zeit. anal. Chem.*, **13**, 272, 1874; A. Carnot, *Compt. rend.*, **102**, 621, 1886; *Bull. Soc. chim.*, (2), **46**, 812, 1886; H. Baubigny, *Compt. rend.*, **142**, 577, 792, 959, 1906; W. Cooper, *Chem. News*, **110**, 250, 1914; L. A. Congdon and R. C. Canter, *ib.*, **128**, 116, 1924; P. N. Das-Gupta and H. Saha, *Journ. Indian Chem. Soc.*, **8**, 19, 1931.

[3] P. von Berg, *Zeit. anal. Chem.*, **26**, 23, 1887; H. Enell, *ib.*, **54**, 537, 1915; E. J. Ericson, *Journ. Ind. Eng. Chem.*, **9**, 671, 1917; L. A. Congdon and R. C. Canter, *Chem. News*, **128**, 116, 1924; E. J. Kraus, *Chem. Ztg.*, **50**, 281, 1926. This process is extensively used for the determination of sulphur in iron and steel. The sample is treated with hydrochloric acid and the evolved hydrogen sulphide passed through a solution of cadmium chloride or acetate, thereby precipitating cadmium sulphide. For alternative volumetric processes for the determination of cadmium, see H. Enell (*l.c.*); R. Cernatesco, *Bull. Acad. Sci. Roumaine*, **8**, 43, 1922; L. A. Congdon and R. C. Canter (*l.c.*); R. C. Wiley, *Ind. Eng. Chem. Anal. Ed.*, **3**, 14, 1931.

[4] 7·917 grms. of iodine, and 16 grms. of potassium iodide per litre. 1 grm. of iodine corresponds with 0·5059 grm. CdO. Hence 1 c.c. of iodine represents 0·001 grm. of sulphur or 0·004005 grm. CdO.

Dilute the solution to about 300 c.c., and titrate the excess of iodine with a standard solution of sodium thiosulphate, as indicated for copper (de Haen's process, page 367).[1]

§ 181. The Electrolytic Determination of Cadmium— Beilstein and Jawein's Process.

The electrolytic process for cadmium (page 255) generally gives more accurate results than gravimetric or volumetric processes. The following method is due to Beilstein and Jawein.[2]

The Electrolyte.—Add a drop of phenolphthalein to a solution of a cadmium salt containing, say, 0·5 grm. of the sulphate or acetate. Then add potassium hydroxide until a permanent red colour is obtained. Cadmium hydroxide is precipitated. Add a solution of 98 per cent. potassium cyanide, slowly, with constant stirring, until the precipitate is all redissolved. An excess of the potassium cyanide disturbs the action.[3] Make the solution up to about 150 c.c.

The Electrolysis.—The solution so prepared is electrolysed in the cold[4] with a current density of 0·5 to 0·7 amp.,[5] and an electrical pressure of 4·6 to 5 volts.[6] In about 6 hours increase the current density to 1·0–1·2 amps., and continue the electrolysis for about an hour.[7] If the electrolysis is finished, stop the current, wash, dry and weigh the deposited metal in the usual way. There is not so much danger of loss by re-solution of the metal when the current is stopped as is the case with copper (page 257).

Preparation of Cadmium Sulphide for Electrolysis.—Cadmium sulphide is usually separated in gravimetric analysis. Dissolve this in nitric acid. Expel

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[1] For the determination of cadmium as phosphate, see E. H. Miller and R. W. Page, *Zeit. anorg. Chem.*, **28**, 233, 1901; M. Austin, *ib.*, **22**, 207, 1899; *Amer. Journ. Science*, (4), **8**, 206, 1899; L. W. Winkler, *Zeit. angew. Chem.*, **34**, 466, 1921; L. A. Congdon and R. C. Canter, *Chem. News*, **128**, 116, 1924: as oxide, M. Muspratt, *Journ. Soc. Chem. Ind.*, **13**, 211, 1894; P. E. Browning and L. C. Jones, *Zeit. anorg. Chem.*, **13**, 10, 1897; *Amer. Journ. Science*, (4), **2**, 269, 1896; A. J. Whittstat, *Chemist-Analyst*, **17**, 21, 1916; L. A. Congdon and R. C. Canter (*l.c.*); as carbonate, E. H. Miller and R. W. Page (*l.c.*); as oxalate, L. A. Congdon and R. C. Canter (*l.c.*); J. Dick, *Zeit. anal. Chem.*, **78**, 414, 1929; as ferrocyanide, G. Luff, *Chem. Ztg.*, **49**, 513, 1925 ; *Zeit. anal. Chem.*, **65**, 97, 1924/25 ; as metal (by distillation), H. ter Meulen and H. J. Ravenswaay, *Rec. Trav. chim.*, **48**, 198, 1929. For precipitation by pyridine, see S. Kragen, *Monats.*, **37**, 391, 1916; G. Rotter, *Zeit. anal. Chem.*, **64**, 102, 1924; G. Spacu and J. Dick, *ib.*, **73**, 279, 1928; by 8-hydroxyquinoline, R. Berg, *ib.*, **71**, 321, 1927; by β-naphthaquinoline, R. Berg and O. Wurm, *Ber.*, **60B**, 1664, 1927. For a review of methods for the determination of cadmium, see K. Heller and F. Machek, *Mikrochem.*, **19**, 147, 1936.

[2] F. Beilstein and L. Jawein, *Ber.*, **12**, 759, 1879; A. L. Davison, *Journ. Amer. Chem. Soc.*, **27**, 1275, 1905; L. G. Kollock and E. F. Smith, *ib.*, **27**, 1527, 1905; W. D. Treadwell and K. S. Guiterman, *Zeit. anal. Chem.*, **52**, 459, 1913; M. Muspratt, *Journ. Soc. Chem. Ind.*, **13**, 211, 1894; S. Avery and B. Dales, *Journ. Amer. Chem. Soc.*, **19**, 379, 1897; F. C. Mathers and H. M. Marble, *Trans. Amer. Electrochem. Soc.*, **25**, 297, 319, 1914; Report, *Journ. Ind. Eng. Chem.*, **7**, 548, 1915; J. Guzmán and P. Poch, *Anales Soc. Espan. Fís. Quím.*, **15**, 235, 1917; E. F. Smith, *Electro-Analysis*, Philadelphia, 91, 1918; E. Büttgenbach, *Zeit. anal. Chem.*, **65**, 452, 1925; A. Jílek and J. Lukas, *Chem. Listy*, **20**, 18, 1926.

[3] E. H. Miller and R. W. Page, *School Mines Quart.*, **22**, 391, 1901; *Zeit. anorg. Chem.*, **28**, 233, 1901.

[4] For hot solutions, 50°–60°, a current density of 0·1–0·3 amp. and 3·3–4·5 volts will require between 5 and 6 hours.

[5] The metal is not all precipitated after 12 hours with a current density of 0·5 amp. If 1 amp. be employed at the start, the deposit is non-coherent, and liable to drop off.

[6] If left overnight, use a current density of 0·06 amp. and 3·2 volts.

[7] Test the solution for cadmium by acidifying a few drops with hydrochloric acid; boil to expel the hydrocyanic acid (note the gas is very poisonous); add a little H_2S water: a yellow precipitate shows that cadmium is still present.

the excess of acid by evaporation. Dissolve the dry residue in water, add potassium hydroxide and then proceed as indicated above.

Removal of the Cadmium from the Electrode.—The removal of cadmium from the cathode presents no particular difficulty. The metal readily dissolves in nitric acid, although it dissolves but slowly in hot hydrochloric and sulphuric acids.

THE DETERMINATION OF ZINC.

§ 182. The Analysis of Silicates containing Zinc Compounds.

IF a silicate containing zinc be treated as indicated for clays,[1] several points require special attention.

Silica Evaporation.—It is highly important to remove all the silica during the evaporation for silica, because, when ammonia is added to a solution containing zinc and silica, in order to remove the iron and alumina,[2] a zinc compound, said to be zinc silicate, will be precipitated. Again, although zinc chloride alone does not volatilise below a red heat, if an acid solution containing zinc and ammonium chlorides be evaporated to dryness, and gradually heated, the chlorides begin to sublime at about 145°. Hence the evaporation of solutions containing silica, zinc and ammonium chlorides should not be finished at temperatures much higher than 100°.

Ammonia Precipitation.—The addition of ammonia to precipitate iron and aluminium hydroxides leads to the simultaneous precipitation of some zinc

Table XLVII.—Contamination of the Ammonia Precipitate by Zinc.

Used.					Zinc found.		
Zinc.	Iron.	NH₄Cl.	Water.	Ammonia solution.	First filtrate.	Second filtrate.	Total zinc.
Per cent.	Per cent.	Grm.	c.c.	c.c.			
60	2	2	33	5	59·10	0·94	60·04
60	2	2	66	5	59·18	0·82	60·00
60	2	2	132	5	59·02	1·03	60·05
60	10	4	66	10	58·87	1·23	60·10
60	10	6	66	10	58·90	1·00	59·90

[1] Zinc ores are usually decomposed by digestion with acids, say, equal volumes of hydrochloric and nitric acids, and heated on a hot plate until red fumes cease to be evolved. Add 3·5 grms. of ammonium chloride, and heat the solution until it becomes thick and pasty. When the mass is nearly dry, add 30 c.c. of hot water. If silica be present, filter and wash thoroughly; if an insoluble residue remains, fuse the ignited mass with a little sodium carbonate, take up the cold residue in dilute hydrochloric acid, and separate the silica by evaporation to dryness in the usual way. Add the acid filtrate from the silica thus separated to the first filtrate.

[2] E. Prost and V. Hassreidter, *Zeit. angew. Chem.*, **5**, 166, 1892; K. Voigt, *ib.*, **26**, 47, 1913; W. G. Waring, *Journ. Amer. Chem. Soc.*, **26**, 4, 1904.

hydroxide,[1] and two, better three, reprecipitations are needed to eliminate the zinc from the ammonia precipitate,[2] even when zinc alone is to be determined. For instance, Waring obtained the results given in Table XLVII. with artificial mixtures of zinc with iron after single and double precipitation of the iron. In the analysis of three different samples of zinc blende, Waring also obtained [3]:

Table XLVIII.—Contamination of the Ammonia Precipitate by Zinc.

Total iron per cent.	Per cent. of zinc.		
	First filtrate.	Second filtrate.	Third filtrate.
8·62	47·20	3·00	0·58
8·75	46·05	4·75	0·40
14·32	16·50	2·05	0·55

It may also be regarded as a general rule that *hydroxides precipitated by ammonia contain silica and phosphates*, unless these substances have been previously removed.[4]

Manganese Precipitation.—If manganese be precipitated, before the zinc, by one of the usual oxidising agents—bromine, hydrogen peroxide, ammonium persulphate—some zinc hydroxide will be precipitated with the manganese hydroxide.[5] According to Waring, in order to prevent the precipitation of zinc with the manganese, it is necessary to separate the latter as hydrated peroxide, and if the separation be effected from ammoniacal solutions, "the solution should be concentrated and contain a large amount of ammonium chloride."

Precipitation of Zinc as Sulphide.—The zinc can be determined either by the volumetric ferrocyanide process, or precipitated as sulphide. White zinc hydrosulphide is precipitated from neutral solutions of zinc salts by means of hydrogen sulphide,[6] but not if much over 4 c.c. hydrochloric acid (sp. gr. 1·12) be present per 100 c.c. It has already been shown, page 271, that the accumulation of acid as a result of the reversible reaction $ZnCl_2 + H_2S \rightleftharpoons ZnS + 2HCl$ causes re-solution of the zinc sulphide as fast as it is precipitated.[7]

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[1] According to G. Bertrand and M. Savillier (*Bull. Soc. chim.*, (4), **1**, 63, 1907), crystals of calcium zincate—$CaH_2Zn_2O_4.4H_2O$—are deposited on boiling an ammoniacal solution of a zinc salt and an excessive proportion of a calcium salt.

[2] W. Funk, *Zeit. angew. Chem.*, **18**, 1687, 1905.

[3] According to L. L. de Koninck and E. von Winiwarter (*Bull. Soc. chim. Belg.*, **26**, 238, 1912) the retention of zinc by ferric oxide is due to the formation of a double hydroxide and not to adsorption. The retention is prevented by adding 5 per cent. of magnesium (as chloride) and sufficient ammonium chloride to prevent the precipitation of the magnesium hydroxide. E. Beyne, *ib.*, **26**, 355, 1912.

[4] For the solubility of zinc hydroxide in ammonia, see W. Bonsdorff, *Zeit. anorg. Chem.*, **41**, 132, 1904.

[5] M. Dittrich and C. Hassel, *Ber.*, **35**, 15, 3266, 1902; H. Baubigny, *Compt. rend.*, **135**, 22, 965, 1902; **136**, 7, 449, 1903; W. G. Waring, *Journ. Amer. Chem. Soc.*, **26**, 4, 1904.

[6] H. Baubigny, *Compt. rend.*, **107**, 1148, 1888; W. Weinicke, *Pogg. Ann.*, **110**, 655, 1860; E. T. Allen and J. L. Crenshaw, *Zeit. anorg. Chem.*, **79**, 125, 1913; A. Villiers, *Bull. Soc. chim.*, (3), **13**, 165, 1895; F. Seeligmann, *Zeit. anal. Chem.*, **53**, 594, 1914; **54**, 104, 1915.

[7] According to S. Glixelli (*Zeit. anorg. Chem.*, **55**, 297, 1907), the theory of the action of hydrogen sulphide on zinc salts does not depend upon equilibrium conditions similar to those indicated on page 272. He says that the reaction $ZnSO_4 + H_2S = ZnS + H_2SO_4$ is not reversible, but that a kind of "false equilibrium" occurs in acid solutions which may be very

By decreasing the concentration of the acid, or replacing it by a weaker acid, all the zinc can eventually be precipitated. Thus the precipitation can be made if sufficient alkali acetate, formate, oxalate or thiocyanate be present to fix the mineral acid by forming alkali chloride, liberating the organic acid. If too little free mineral acid be present, a condition which may be produced by adding too much alkali acetate, etc., some nickel or cobalt sulphide may be precipitated. Hence careful adjustment of the acidity of the solution is essential for the successful separation of zinc from cobalt or nickel—if too much mineral acid be present (*i.e.* too little alkali acetate, etc., be added) some zinc will remain in solution. Conversely, if too little mineral acid be present (*i.e.* too much alkali acetate, etc., be added) some nickel or cobalt sulphide will be precipitated with the zinc.[1] Many organic acids may be present in relatively large quantities without interfering with the precipitation of the sulphide. This is the case, for instance, with formic, acetic, citric, succinic and chloracetic acids. That acid is best which allows the greatest margin of error between the two extremes.

§ 183. The Theory of the Basic Acetate Separation.

It may now be well to recapitulate our treatment of a complex mixture of colouring oxides with a silicate. The acidified filtrate from the silica was treated with hydrogen sulphide. Lead, bismuth, copper, cadmium, mercury, arsenic, antimony and tin sulphides were precipitated. The filtrate was boiled to expel the hydrogen sulphide and treated with an excess of ammonium chloride and ammonia, when aluminium, titanium and ferric hydroxides were precipitated.[2] Instead of using ammonia as precipitating agent, many prefer the so-called basic acetate separation of iron and aluminium from zinc, manganese, cobalt and nickel. This separation depends upon the fact that solutions of acetates of iron, aluminium, titanium, chromium, zirconium and vanadium are decomposed (page 162) when heated, and insoluble basic acetates are deposited. On the contrary, the acetates of magnesium, manganese, zinc, nickel and cobalt are stable enough to remain undecomposed when their solutions are boiled for a few minutes.[3]

When sodium carbonate is added to a solution of ferric chloride, the precipitate first formed dissolves in the ferric chloride. One part of ferric chloride will dissolve approximately ten parts of ferric hydroxide.[4] Any further addition of sodium carbonate produces a permanent precipitate, since the ferric chloride is already saturated with the hydroxide. If a solution of ferric chloride, just saturated with the hydroxide, be heated, the mixture decomposes and

persistent. According to W. Dederichs (*Pharm. Ztg.*, **44**, 198, 1899), 2 to 3 per cent. of hydrochloric acid must be present to prevent loss of zinc during the precipitation of copper sulphide. For the theory of false equilibrium, see J. W. Mellor, *Chemical Statics and Dynamics*, London, 417, 1904. Glixelli's view does not include all the facts. The precipitated zinc sulphide probably changes into a less soluble form; *vide* page 415. L. Bruner, *Bull. Acad. Sci. Cracow*, 603, 1906; G. Bruni and M. Padoa, *Atti R. Accad. Lincei*, (5), **14**, ii, 525, 1905.

[1] For the precipitation of zinc as sulphide in the presence of manganese, cobalt and nickel, see E. A. Ostroumov, *Ann. Chim. anal. Chim. appl.*, **19**, 145, 1937.

[2] We ignore *pro tempore* the possible occurrence of certain constituents in both the hydrogen sulphide and the ammonia groups.

[3] Formates, succinates and benzoates have been suggested in place of the acetates since they can be more readily filtered and washed, but it is generally said that the precipitations are not then so complete. For instance, chromium is not precipitated with the formates unless an excess of iron is present (F. Schulze, *Chem. Centr.*, (2), **6**, 3, 1861; O. F. Tower, *Journ. Amer. Chem. Soc.*, **32**, 933, 1910; W. Hisinger, *Afhandlingar i Fysik*, **3**, 153, 1810).

[4] F. Kessler, *Zeit. anal. Chem.*, **11**, 258, 1872; **18**, 8, 1879; *Chem. News*, **27**, 14, 1873.

ferric hydroxide is precipitated. If sodium or ammonium acetate be added to a solution of ferric hydroxide in ferric chloride, ferric acetate is produced. This is hydrolysed on heating and a basic ferric acetate is precipitated, while acetic acid passes into solution.

The hydrolysis (page 162) which occurs on boiling is only completed in dilute solutions—at least 500 c.c. of water should be present per gram of ferric hydroxide. For complete precipitation, therefore, as much sodium carbonate should be added as is possible without causing a permanent precipitate; and only sufficient sodium acetate should be added to replace the combined chlorine of the ferric chloride in solution.

If a mixture of aluminium, ferric, nickel, manganese, zinc and cobalt salts be so treated, the acetates of manganese, zinc, cobalt and nickel are hydrolysed at a much higher temperature (175°) than the aluminium and ferric acetates. If a large excess of alkali acetate be present, the acetates of manganese, nickel, cobalt and zinc are decomposed at a much lower temperature, and they may, in consequence, be precipitated along with the iron and aluminium on boiling the solution. Manganese acetate does not appear to be hydrolysed under these conditions when less than twenty times the required amount of alkali acetate is present; nickel acetate is more liable to hydrolysis than cobalt; while zinc is next to manganese in its tendency to hydrolyse and form the hydroxide or basic acetate and free acetic acid.[1]

Acetic acid is usually added to the solution *before* the alkali acetate in order to lessen the danger of the joint precipitation of manganese, zinc, cobalt and nickel along with the aluminium and iron. But since aluminium hydroxide (and phosphate) is soluble in dilute acetic acid, and since alumina usually predominates in silicate analyses, while zinc, nickel and cobalt, if present at all, only occur in minute quantities, it is best to work with as little free acetic acid as possible when dealing with clays and related substances. The presence of 11 per cent. of acetic acid will prevent the precipitation of the iron and 5 per cent. will prevent the precipitation of aluminium. In illustration, two solutions containing the equivalent of 0·2 grm. of iron, and 0·2 grm. each of manganese, zinc, nickel and cobalt, were mixed with 2 grms. of sodium acetate, and each made up to 300 c.c.; 12 c.c. and 3 c.c. of acetic acid (sp. gr. 1·044) were added, so that the solutions contained, respectively, 4 per cent. and 1 per cent. by volume of acetic acid. After treatment by the basic acetate process, the precipitate, according to Brearley, contained the equivalent of

Acetic acid.	Manganese.	Zinc.	Nickel.	Cobalt.
1 per cent. . . .	0·0585	0·2046	0·1770	0·0590
4 per cent. . . .	trace	nil	0·1219	0·0315

[1] A. Mittasch, *Zeit. anal. Chem.*, 42, 492, 1903; W. Funk, *ib.*, 45, 181, 1906; C. Stöckmann, *ib.*, 16, 172, 1877; C. Kramer, *ib.*, 16, 334, 1877; G. Matzurke, *ib.*, 17, 78, 1878; O. Brunck, *Chem. Ztg.*, 28, 511, 1904; G. Rosenthal, *Dingler's Journ.*, 225, 154, 1877; C. Meineke, *Zeit. angew. Chem.*, 1, 224, 1888; J. Jewett, *Amer. Chem. Journ.*, 1, 251, 1879; *Chem. News*, 40, 273, 1879; H. Brearley, *ib.*, 75, 13, 1897; 76, 165, 222, 1897; 79, 193, 1899; A. Jeannel, *ib.*, 17, 286, 1868; T. Moore, *ib.*, 56, 75, 1887; R. L. Leffler, *ib.*, 77, 265, 1898; J. B. Mackintosh, *ib.*, 56, 64, 1887; W. Gibbs, *ib.*, 11, 102, 1865; *Amer. J. Science*, (2), 39, 58, 1865; W. Herz, *Zeit. anorg. Chem.*, 20, 16, 1899; B. Reinitzer, *Monats.*, 3, 256, 1882; G. Rudorf, *Zeit. phys. Chem.*, 43, 262, 1903; V. von Eggertz, *Berg. Hütt. Ztg.*, 26, 187, 1867; W. Hampe, *Zeit. Berg. Hütt. Sal.*, 25, 253, 1877; F. Mayer, *Ber.*, 22, 2627, 1889; R. B. Riggs, *Journ. Anal. App. Chem.*, 6, 94, 1892; R. F. Weinland and E. Gussmann, *Zeit. anorg. Chem.*, 66, 157, 1910; G. van Pelt, *Bull. Soc. chim. Belg.*, 28, 101, 138, 1914; L. Blum, *Stahl Eisen*, 34, 489, 1914; A. Charriou, *Compt. rend.*, 175, 693, 1922; A. Kling and A. Lassieur, *ib.*, 178, 1551, 1924. P. Wenger, C. Cimerman and M. Gorni (*Compt. rend. Soc. Phys. Hist. nat. Genève*, 50, 157, 1933) say that iron should be precipitated at a p_H less than 6, the optimum value being 4·2.

The precipitate by the basic acetate process contains titanium, most of the zirconium,[1] vanadium, uranium,[2] as well as phosphorus [3] and arsenic, if present. Chromium (*q.v.*) is precipitated with the iron and aluminium, but the separation is not satisfactory with chromium. This process can also be used for separating iron and aluminium from the rare earths.[4]

The basic acetate process requires careful manipulation when much manganese, nickel and cobalt are present. Any method of analysis which depends for its completion on a careful adjustment of the composition of the solution, as is here indicated, cannot be a safe general method. A second application of the process is often advised, by redissolving the precipitate in hydrochloric acid. Moore says four precipitations are necessary, Mackintosh says six! If the process be conducted with due respect for the idiosyncrasies indicated above, two acetate precipitations, or one acetate precipitation followed by an ammonia precipitation, will generally suffice. Practical directions for the process now follow.

§ 184. The Basic Acetate Separation.

Neutralisation of the Solution.—Gradually add a concentrated aqueous solution of sodium carbonate from a burette, with constant stirring, until the precipitate begins to disappear slowly [5]; then add a dilute solution in a similar way until the small precipitate does not disappear with one or two minutes' stirring. If much iron be present, the solution will now have a reddish tint; but if little iron be present, the solution will be almost colourless. Add 3 c.c. of acetic acid (sp. gr. 1·044) to dissolve the precipitate, and allow the solution to stand a couple of minutes.[6] If the solution be not clear, add another drop of dilute acetic acid, and proceed as before. If necessary, repeat the addition of dilute acetic acid, drop by drop, until the solution does become clear under the conditions stated.

Precipitation.—Dilute the solution to about 400 c.c. and heat to boiling; add about 6 c.c. of sodium acetate solution.[7] Do not boil the mixture more than

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[1] E. Linnemann (*Monats.*, 6, 335, 1885) says the separation is not complete.

[2] H. Rheineck, *Chem. News*, 24, 233, 1871.

[3] If phosphates and vanadates be present in preponderating quantity, the method of separation breaks down, since insoluble compounds are formed with any manganese present—G. E. F. Lundell and H. B. Knowles, *Journ. Amer. Chem. Soc.*, 45, 676, 1923.

[4] A. Beringer, *Liebig's Ann.*, 42, 134, 1842; T. Scheerer, *Pogg. Ann.*, 51, 467, 1840.

[5] According to H. Tamm (*Chem. News*, 26, 37, 1872), oxidation with nitric acid leads to the precipitation of manganese with the iron and alumina. It is claimed that the oxidation of the iron is best effected with potassium chlorate. According to M. Carus (*Chem. Ztg.*, 45, 1194, 1921), the contamination of the basic acetate precipitate by manganese is due not to co-precipitation but to the formation of higher oxidation products of manganese, owing to the action of dissolved oxygen. A perfect separation with one precipitation, even in the presence of excess of manganese, is claimed by adding 3 c.c. of 3 per cent. hydrogen peroxide before the sodium acetate. The higher manganese compounds are reduced to the manganous state and as such are soluble in the acetic acid.

[6] Some add 3 c.c. of acetic acid (sp. gr. 1·044; that is, 33 per cent.) in excess, for every 100 c.c. of solution in the beaker previous to the dilution. As indicated in the text, an excess of acid, however, leads to an incomplete precipitation of the aluminium, while too little acid will lead to the precipitation of manganese, zinc, nickel and cobalt, if these elements be present.

[7] SODIUM ACETATE SOLUTION.—Dissolve 167 grms. of sodium acetate in water and make the solution up to 500 c.c. One c.c. of this solution will contain one-third of a gram of sodium acetate. Ammonium acetate is not so suited for the work, although it is sometimes recommended, chiefly because it is removed from the precipitate on ignition. Ammonium acetate has the disadvantage of being more readily hydrolysed (page 162) than sodium acetate in aqueous solution. H. C. Dibbits (*Bull. Soc. chim.*, (2), 18, 490, 1872; (2), 20, 258, 1873) says that 7·6 per cent. of ammonium acetate is hydrolysed against 0·14 per cent. of sodium acetate. Hence, on boiling solutions of ammonium acetate, ammonia is evolved

a minute, or the precipitate will become slimy, and some may dissolve in the acetic acid. The precipitate is bulky and difficult to filter [1] and wash. Filter and wash with hot water containing 50 grms. of sodium acetate per litre.[2] Suck the precipitate dry at the pump, using a platinum filter cone (page 88) to support the filter-paper. The precipitate is seldom or never ignited and weighed because it is always contaminated with alkali salts. Hence it must be dissolved in nitric or hydrochloric acid and reprecipitated with ammonia, as described on page 165.

The process just outlined gives satisfactory results. The presence of sulphates, however, leads to imperfect precipitations.[3] Tartaric and citric acids should be absent. Indeed, it might here be emphasised that analysts are very chary about introducing organic acids into their solutions, because, if later separations have to be made, there is some uncertainty as to the effect of the organic acids on subsequent precipitations. Tartaric, citric, oxalic, malic and other organic acids, dextrin and the sugars, for instance, prevent the precipitation of aluminium, chromium and ferric hydroxides by ammonia [4]; and of manganese sulphide by ammonium sulphide.[5]

Evaporate the combined filtrates to about 200 c.c. If a precipitate should separate, filter it off, dissolve the precipitate in hydrochloric acid and precipitate the iron and alumina in the solution as basic acetates; add the filtrates to the main filtrate.

Suppose that zinc, cobalt and nickel be absent; the manganese may now be precipitated by a number of different processes, e.g. by bromine or by ammonium sulphide. If cobalt, nickel and zinc be present, first remove the zinc by the formic acid process described below.

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and the solution becomes more acid. Thus the acidity of solutions of ammonium acetate is less easy to control than solutions of sodium acetate. W. Gibbs (Chem. News, 11, 102, 1865) adds the acetate to the cold solution and then heats the solution to boiling. H. Brearley (ib., 79, 193, 1899) says a large excess of acetate always leads to an imperfect separation of, say, nickel and iron, because (1) the excess of acetate transforms the nickel as well as iron into acetate; and (2) the nickel acetate is partially decomposed along with the ferric acetate. "When the acetate is added to the cold solution, both these factors exert their maximum influence. On adding acetate to the boiling solution, the first portion of it precipitates the iron; when the remaining portion is added, the conditions are changed, for the iron is present in suspension only, and its influence is greatly lessened."

[1] H. N. Warren (Chem. News, 61, 63, 1890) agitates finely powdered glass with the precipitate. He claims that if this is properly done, the glass carries down the precipitate and enables the washing to be done more quickly. The glass does no harm, since the precipitate is afterwards dissolved in acid. A. Kling and A. Lassieur (Compt. rend., 178, 1551, 1924) add paper pulp before precipitation.

[2] The filtrate may be tested for iron by potassium ferrocyanide, not thiocyanate.

[3] Sulphates must not be determined in the filtrate from the basic acetate process on account of the great probability of contamination with sulphates from the large amounts of reagents used.

[4] M. Juette, Compt. rend., 66, 417, 1868; Chem. News, 18, 63, 1868; J. Roszkowski, Zeit. anorg. Chem., 14, 1, 1897; C. Aubel and G. Ramdohr, Journ. prakt. Chem., (1), 72, 184, 1857; Liebig's Ann., 103, 33, 1857; J. Löwe, Zeit. anal. Chem., 9, 20, 1870; J. Puls, Journ. prakt. Chem., (2), 15, 83, 1877; H. Grothe, ib., (1), 92, 175, 1864; C. Claus, ib., (2), 4, 63, 1871; Corey, Diss., Zurich, 1868; E. Salkowski, Pfluger's Archiv, 6, 221, 1885; M. F. Pisani, Compt. rend., 45, 349, 1857; W. Weith, Ber., 9, 342, 1876; L. Dossios, Liebig's Ann., 146, 174, 1868; F. Hofmeister, ib., 189, 6, 1877; G. Städeler and W. Krause, Jahrb., 746, 1854; L. Kahlenberg, Zeit. phys. Chem., 17, 577, 1895.

[5] J. Spiller, Journ. Chem. Soc., 10, 110, 1858; Chem. News, 8, 280, 1863; 19, 166, 1869; H. How, ib., 19, 137, 1869; H. N. Draper, ib., 8, 260, 1863; F. Field, ib., 3, 65, 1861; M. F. Pisani, ib., 3, 257, 1861; L. J. Curtman and H. Dubin, Journ. Amer. Chem. Soc., 34, 1485, 1912; E. Salkowski, Zeit. physiol. Chem., 83, 159, 1913.

§ 185. The Separation of Zinc from Manganese, Cobalt and Nickel.

Assume that the filtrate from the ammonia or basic acetate separation contains zinc,[1] manganese,[2] cobalt and nickel, as well as magnesia, lime and the alkalies.

Precipitation of Zinc Sulphide.—The ammoniacal solution is neutralised with formic acid, and about 5 c.c. additional formic acid (sp. gr. 1·2) is added per 150 c.c. of solution. Not more than about 3 per cent. excess of formic acid should be present, or some of the zinc may escape precipitation. Enough sodium formate should be present to react with the inorganic acids set free by the action of the hydrogen sulphide, and so prevent free hydrochloric acid accumulating in the solution.[3] Heat the solution to 50°-60°. Pass hydrogen sulphide (two bubbles a second) through the warm solution for an hour in order that the zinc sulphide may coagulate and filter quickly.[4] Zinc sulphide is

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[1] Zinc may be found in reagents kept in Jena and "nonsol" glass bottles, page 127. Acids transported in carboys with glass covers secured by zinc rings are liable to contamination owing to the splashing of the acid into the neck of the carboy. This explains how zinc has been reported when no zinc was present in the original sample. A. Vita, *Stahl Eisen*, **32**, 1532, 1912; *Sprech.*, **42**, 787, 1912.

[2] The manganese may or may not have been removed prior to the zinc.

[3] W. Hampe, *Chem. Ztg.*, **9**, 543, 1885; *Chem. News*, **52**, 313, 1885; M. Bragard, *Chem. Ztg.*, **10**, 729, 1886; E. Dohler, *ib.*, **23**, 399, 1899; P. von Berg, *Zeit. anal. Chem.*, **25**, 512, 1886; G. Naumann, *ib.*, **28**, 57, 1889; W. Funk, *ib.*, **46**, 93, 1907; H. Kinder, *Stahl Eisen*, **16**, 675, 1896; F. W. H. Delffs, *Zeit. Chem. Pharm.*, **3**, 4, 1860; *Chem. News*, **41**, 279, 1880; T. Cockburn, A. D. Gardiner and J. W. Black, *Analyst*, **37**, 443, 1912. According to Bragard, the solution should have 5 c.c. of formic acid (sp. gr. 1·1136) per 0·03 grm. of nickel in solution, and this amount should not be exceeded if the zinc is to be precipitated completely. If much nickel be present, the solution should be diluted to 500-600 c.c. If the solution be heated, more acid is needed to prevent the precipitation than if the solution be "gassed" cold. A very slight excess of hydrochloric acid added to a neutral solution is sometimes used instead of formic acid, but there is a difficulty in regulating the correct amount of acid, and the results are satisfactory when only small amounts of zinc are present. C. Brunner, *Dingler's Journ.*, **150**, 369, 1858; A. Klaye and A. Deus, *Zeit. anal. Chem.*, **10**, 190, 1871; F. Oettel, *ib.*, **27**, 16, 1888; J. B. Kirkland, *Rep. Australasian Assoc.*, **2**, 397, 1890. For the separation in the presence of free mineral acids, see I. Majdel, *Arhiv. hem. Pharm.*, **2**, 127, 1928; *Zeit. anal. Chem.*, **76**, 204, 1929; O. Ruff and B. Hirsch, *Zeit. anorg. Chem.*, **150**, 84, 1925; H. Katô, *Journ. Chem. Soc. Japan*, **54**, 867, 1933. For acetic acid, see A. Rosenheim and E. Huldschinsky, *Zeit. anorg. Chem.*, **32**, 84, 1902; A. Thiel, *ib.*, **33**, 1, 1902; H. Nissenson and W. Kettembeil, *Chem. Ztg.*, **29**, 950, 1905; J. Flath, *ib.*, **25**, 564, 1901; W. G. Waring, *Journ. Amer. Chem. Soc.*, **26**, 4, 1904; W. Funk, *Zeit. anal. Chem.*, **46**, 104, 1907; M. Bragard, *ib.*, **26**, 209, 1887; H. Kinder, *Stahl Eisen*, **16**, 675, 1896; J. Platz, *ib.*, **9**, 494, 1889; H. Baubigny, *Compt. rend.*, **108**, 236, 450, 1888; G. Jander and H. C. Stuhlmann, *Zeit. anal. Chem.*, **60**, 289, 1921; K. Bornemann, *Zeit. anorg. Chem.*, **82**, 216, 1913. For citric acid, see F. Beilstein, *Ber.*, **11**, 1715, 1878; E. E. Marbaker, *Journ. Amer. Cer. Soc.*, **14**, 162, 1931; F. G. Hills, *Ind. Eng. Chem. Anal. Ed.*, **5**, 201, 1933. For oxalic acid, A. Carnot, *Compt. rend.*, **102**, 678, 1886. For succinic acid, H. Alt and J. Schultze, *Ber.*, **22**, 3259, 1889; H. Delffs, *Chem. News*, **41**, 279, 1880. For monochloracetic acid, P. von Berg, *Zeit. anal. Chem.*, **25**, 512, 1886; H. Katô, *Journ. Chem. Soc. Japan*, **55**, 213, 1934; E. A. Ostroumov, *Ann. Chim. anal. Chim. appl.*, **19**, 145, 1937. For trichloracetic acid, J. J. Fox, *Journ. Chem. Soc.*, **91**, 964, 1907. It is claimed that this acid is better for the separation of zinc and cadmium, since the acidity limits are not so narrow as with hydrochloric acid. For benzene monosulphonic acid, see H. Schilling, *Chem. Ztg.*, **36**, 1352, 1912. For thiocyanic acid, see C. Zimmermann, *Liebig's Ann.*, **199**, 3, 1879; **204**, 226, 1880; F. D. Treadwell, *Zeit. anorg. Chem.*, **26**, 104, 1901.

[4] Zinc sulphide is a difficult precipitate to filter and wash. It may be gelatinous or in a very finely divided condition suspended in the fluid; in the former case washing is very slow; in the latter case the precipitate passes through the paper (pages 160 and 274)—A. Villiers, *Compt. rend.*, **120**, 97, 188, 322, 498, 1895. P. Pipereaut and A. A. Vila (*Internat. Cong. App. Chem.*, **7**, i, 141, 1909) say that zinc sulphide is precipitated in a very dense form,

practically insoluble in formic acid of the strength just indicated; and, like many other sulphides, changes from the colloidal form after precipitation. Hence it is better to let the mixture stand overnight in a warm place with a slow current of hydrogen sulphide passing through the solution, or else let it stand some time in a corked flask. The larger the excess of formic acid, the slower the separation of the zinc sulphide, and the larger the excess of alkali acetates or formates present, the more slimy the precipitated sulphide and the more difficult it is to filter and wash.

Filtering and Washing the Zinc Sulphide. — Filter off the precipitated sulphide and test the filtrate with hydrogen sulphide to make sure that all the zinc is precipitated. Wash the precipitate thoroughly two or three times with water saturated with hydrogen sulphide, and containing a little formic acid. Collect the washings in separate beakers, so that if the filtrate should begin to run through turbid,[1] as sometimes occurs when the ammonium salts are nearly all washed out, it will not be necessary to re-filter a large quantity of liquid. The precipitate is usually free from manganese, cobalt and nickel if the solution has 15–20 c.c. of formic acid (sp. gr. 1·2) per 250–500 c.c. When a relatively large amount of these elements is present the precipitate may be contaminated, and it is advisable to dissolve the precipitate in dilute hydrochloric acid, neutralise with ammonia and reprecipitate with hydrogen sulphide. Add the second filtrate to the first. The joint filtrates are reserved for the separation of manganese, cobalt and nickel, as indicated on page 415. The precipitate of zinc sulphide is then treated as indicated in the next section.

Influence of Formic Acid.—To illustrate the relation between the amount of acid in the solution and the efficiency of the formic acid separation, the following numbers are quoted from Bragard's work:—

Table XLIX.—Effect of Formic Acid on the Separation of Zinc and Nickel as Sulphides.

Zinc.	Nickel.	Volume solution.	Formic acid.	Zinc pptd.	Nickel pptd. with zinc.
grm.	grm.	c.c.	c.c.	grm.	per cent.
0·0325	0·0048	300	5	0·0324	54·2
0·0325	0·0048	300	6	0·0325	37·5
0·0325	0·0048	300	7	0·0322	22·9
0·0325	0·0048	300	10	0·0325	0·0
0·0325	0·0096	500	10	0·0325	0·0
0·3252	0·0960	400	10	0·3252	28·1
0·3252	0·0960	500	20	0·3247	18·4
0·3252	0·0960	600	30	0·3252	8·0
0·3252	0·0960	600	40	0·3248	0·0

readily washed, by the addition of finely divided sulphur to the boiling alkaline solution. The precipitate is white, and when the precipitation is complete, a pink coloration appears. E. Murmann (*Monats.*, 19, 404, 1898) adds a little mercuric chloride to the solution before "gassing." The results are good. See page 328. G. Jander and H. C. Stuhlmann (*loc. cit.*) and W. Awe (*Arch. Pharm.*, 265, 147, 1927) collect the zinc sulphide on a membrane filter. For the precipitation in the presence of sodium bisulphite, see K. Bornemann, *loc. cit.* H. A. Fales and G. M. Ware (*Journ. Amer. Chem. Soc.*, 41, 487, 1919) say that a granular precipitate is obtained by using a solution having a high concentration of the ammonium salt of a strong acid (sulphuric).

[1] O. Mühlhauser, *Zeit. angew. Chem.*, 15, 731, 1902.

The 1904 report of the Committee on Uniformity in Technical Analyses [1] shows analyses of three samples of zinc ore by forty-two chemists. As a result:

	SAMPLE A.		SAMPLE B.		SAMPLE C.	
	Zn.	Fe.	Zn.	Fe.	Zn.	Fe.
Highest results . . .	39·22	21·92	38·86	15·00	59·79	3·26
Lowest results . . .	12·20	18·04	28·90	8·40	56·03	2·10

The results for samples A and B are surprisingly discordant, and seriously undermine confidence in many published analyses. Each chemist used the particular process he thought best.

§ 186. The Determination of Zinc as Phosphate.

Zinc sulphide is not an easy precipitate to prepare for the balance and, in consequence, many adopt Tamm's [2] process, in which the zinc is precipitated as phosphate. This is an easy gravimetric process, although, in practice, with the standard solutions ready made, it is far easier to get good results with the unwashed sulphide by volumetric processes than by gravimetric methods which involve the washing of the precipitated zinc sulphide.

Effect of Alkali Salts.—If the solution contains sodium or potassium salts, the precipitate will be contaminated with zinc sodium phosphate, $ZnNaPO_4$, and zinc potassium phosphate, $ZnKPO_4$.[3] In the presence of sodium salts correct results are given by precipitation with secondary ammonium phosphate, $(NH_4)_2HPO_4$, in neutral solution after the addition of 5–10 grms. of ammonium chloride.[4] A second precipitation is necessary if potassium salts are present, ammonium chloride being added before each precipitation.

Dissolve the precipitated sulphide in hot dilute hydrochloric or nitric acid. Boil the solution to expel the hydrogen sulphide. Filter off any sulphur which separates. The acid solution, occupying about 150 or 200 c.c.,[5] is neutralised with ammonia and then made faintly acid with hydrochloric acid. Add about 2 grms. of ammonium chloride for each 0·1 grm. of zinc. Heat

[1] *Journ. Amer. Chem. Soc.*, **26**, 1644, 1904.

[2] H. Tamm, *Chem. News*, **24**, 148, 1871; G. Lösekann and T. Mayer, *Chem. Ztg.*, **10**, 729, 1886; L. Jawein, *ib.*, **11**, 347, 1887; M. Bragard, *ib.*, **10**, 1605, 1886; G. C. Stone, *Journ. Amer. Chem. Soc.*, **4**, 26, 1882; R. W. Langley, *ib.*, **31**, 1051, 1909; A. C. Langmuir, *ib.*, **21**, 125, 1899; *Chem. News*, **79**, 183, 1899; H. D. Dakin, *Zeit. anal. Chem.*, **39**, 273, 1900; *Chem. News*, **82**, 101, 1900; M. Austin, *Amer. J. Science*, (4), **8**, 206, 1899; R. C. Boyd, *School Mines Quart.*, **11**, 355, 1890; J. Clark, *Journ. Soc. Chem. Ind.*, **15**, 866, 1896; M. Pouget, *Compt. rend.*, **129**, 45, 1899; K. Voigt, *Zeit. angew. Chem.*, **22**, 2280, 1909; **24**, 2195, 1911; **25**, 205, 1912; V. Hassreidter, *ib.*, **24**, 2491, 1911; **25**, 1005, 1912; K. Voigt, *ib.*, **26**, 47, 1913; Report in *Journ. Ind. Eng. Chem.*, **4**, 467, 1912; P. Artmann, *Zeit. anal. Chem.*, **54**, 89, 1915; **62**, 8, 1923; D. Balareff, *ib.*, **60**, 442, 1921; P. Artmann and W. Hartmann, *ib.*, **62**, 17, 1923; L. W. Winkler, *Zeit. angew. Chem.*, **34**, 235, 1921; R. Strebinger and J. Pollak, *Mikrochem.*, **4**, 15, 1926; L. A. Congdon, A. B. Guss and F. A. Winter, *Chem. News*, **131**, 65, 81, 97, 113, 1925; L. Hahn and J. Dornauf, *Ber.*, **55B**, 3434, 1922.

[3] T. M. Finlay and A. C. Cumming, *Journ. Chem. Soc.*, **103**, 1004, 1913.

[4] L. Dede (*Ber.*, **61B**, 2463, 1928) says the results are inaccurate when more than 3 per cent. of sodium chloride is present and recommends precipitating the excess of sodium chloride by passing hydrogen chloride through the concentrated solution. The precipitate is then filtered off and washed with highly concentrated hydrochloric acid, the excess of acid being removed from the filtrate by evaporation to dryness.

[5] The solution is diluted so as to contain 0·2 to 0·4 grm. zinc per 400 c.c. of solution.

the solution to boiling, add 15 to 20 times as much secondary ammonium phosphate [1] as there is zinc in the solution. If a precipitate does not form, carefully add ammonia until it does.[2] The solution will now be alkaline. Keep the vessel and contents warm on a water bath for 10-15 minutes and the amorphous ammonium zinc phosphate—$ZnNH_4PO_4$—first precipitated will crystallise. If the solution be boiled it bumps badly. Let the precipitate settle.[3] When cold, filter through asbestos [4] in a Gooch crucible. Clean [5] the beaker with the mother liquid, and wash with cold water containing about 1 per cent. of ammonium phosphate until the precipitate is free from chlorides, then wash with a dilute solution of ammonium nitrate until free from phosphates. Finish the washing with alcohol. Dry at 100°, and weigh the precipitate as $ZnNH_4PO_4$. This weight, when multiplied by 0·4561, represents the corresponding amount of zinc oxide—ZnO.[6]

The precipitate can also be ignited to low redness and weighed as zinc pyrophosphate—$Zn_2P_2O_7$. If the ignition be conducted at too high a temperature, the pyrophosphate may melt and be absorbed by the asbestos, with but a slight loss in weight—possibly 0·1 per cent. The weight of the pyrophosphate multiplied by 0·5340 gives the corresponding amount of zinc oxide—ZnO.

§ 187. The Volumetric Ferrocyanide Process for Zinc.

Zinc ferrocyanide is precipitated from a hydrochloric acid solution of a zinc salt by potassium ferrocyanide. When all the zinc has been converted into zinc ferrocyanide, any further addition of the potassium ferrocyanide will cause the solution to give a brown coloration with a uranium salt.[7]

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[1] P. Artmann (*Zeit. anal. Chem.*, 62, 8, 1923) uses an excess of at least 10 c.c. of 3N-ammonium phosphate per 150 c.c., so that after precipitation the solution is not less than N/5 in ammonium phosphate. If microcosmic salt be used, there is more difficulty in washing the precipitate free from alkalies than when the ammonium salt is used.

[2] The precipitate is soluble in acids and ammonia, and slightly soluble in large quantities of ammonium salts. G. Luff (*Chem. Ztg.*, 46, 365, 1922) accordingly separates aluminium and iron as phosphates from zinc in acetic acid solution and, similarly, magnesium and manganese in ammoniacal solution. For chromium phosphate, see H. Kämmerer, *Zeit. anal. Chem.*, 12, 375, 1873.

[3] The important points to observe in precipitation are a large excess of reagent and sufficient ammonium salts to flocculate the precipitate; if too great an excess of ammonium salts be present, a little zinc phosphate may pass into solution. If, in addition to alkali salts, other metals be present, the precipitate may be contaminated accordingly.

[4] A slight loss of zinc by reduction to metal, with subsequent volatilisation, may occur if filter-paper be used and the precipitate be afterwards ignited. If the precipitate be ignited, the asbestos used in the Gooch crucible should have been previously calcined. Otherwise, drying at 100° will suffice.

[5] The precipitate is inclined to stick tenaciously to the walls of the beaker in which the precipitation is made. It may then be necessary to dissolve the precipitate from the walls with a little acid and evaporate to dryness in a weighed crucible.

[6] Tests made under various conditions show that here less than 0·0003 grm. of zinc phosphate escapes with the filtrate and in the washings. P. Artmann (*Zeit. anal. Chem.*, 54, 89, 1915) gives the solubility of zinc ammonium phosphate as 1·45 mgrm. per 100 c.c. of water at 17·5° and corrects the results accordingly from the volume of the filtrate. For about 0·3 grm. of precipitate L. W. Winkler (*loc. cit.*) adds 0·3 mgrm. to the weight of $ZnNH_4PO_4$ or 0·9 mgrm. to that of $Zn_2P_2O_7$.

[7] E. H. Miller, *Journ. Amer. Chem. Soc.*, 18, 1100, 1896; 22, 541, 1900; 24, 226, 1902; E. H. Miller and J. A. Matthews, *ib.*, 19, 547, 1897; E. H. Miller and M. J. Falk, *ib.*, 26, 952, 1904; E. H. Miller and J. L. Danziger, *ib.*, 24, 827, 1902; G. C. Stone and D. A. van Ingen, *ib.*, 19, 542, 1897; E. H. Miller and E. J. Hall, *School Mines Quart.*, 21, 267, 1900; *Chem. News*, 82, 177, 1900; F. Reindel, *Dingler's Journ.*, 190, 395, 1868; K. Zulkowsky, *ib.*, 249, 175, 1893; M. Bragard, *Beiträge zur Kenntnis der quantitativen Bestimmung des Zinks*, Berlin, 1887; G. Wyrouboff, *Ann. Chim. Phys.*, (5), 8, 444, 1876; L. L. de Koninck and E. Prost, *Zeit. angew. Chem.*, 9, 460, 564, 1896; *Chem. News*, 76, 6, 15, 29, 38, 51, 1897.

Theory of Process.—If the ferrocyanide be gradually added to the solution, there is first a slow formation of normal zinc ferrocyanide:

$$2ZnCl_2 + K_4Fe(CN)_6 \rightarrow 4KCl + Zn_2Fe(CN)_6$$

If the solution be cold (20° to 25°), it will at first colour a drop of uranium nitrate a fading yellowish-brown. When about three-quarters of the required amount of potassium ferrocyanide has been added, the solution no longer affects the indicator—uranium salt. The precipitate becomes flocculent. The slow reaction just indicated is followed by a faster reaction:

$$3Zn_2Fe(CN)_6 + K_4Fe(CN)_6 \rightarrow 2K_2Zn_3[Fe(CN)_6]_2$$

The indicator is coloured permanently when the second reaction is completed. The whole reaction is therefore written:

$$3ZnCl_2 + 2K_4Fe(CN)_6 \rightarrow Zn_3K_2[Fe(CN)_6]_2 + 6KCl$$

After a little practice, the transient colour first produced will not be mistaken for the final permanent coloration. The first coloration gradually fades and the permanent tint becomes more intense. The solution during the former stage is bluish-white and during the latter stage pale cream. The first transient coloration of the indicator does not appear if the solutions be hot, because the first reaction proceeds quickly. This reaction is the basis of Galetti's process [1] for the volumetric determination of zinc. If the process be carried out in a regular, uniform manner, comparable and satisfactory results can be obtained. "In my opinion," says Seaman, "the results for zinc by the ferrocyanide process more nearly approach the absolute amount of zinc in an ore than the results obtained by working slowly with the gravimetric process."

Disturbing Agents.—Anything which oxidises or decomposes the ferrocyanide solution should be absent, such as strong acids or chlorine. Metals

[1] M. Galetti, *Zeit. anal. Chem.*, 4, 213, 1865; 8, 135, 1869; 14, 190, 1875; *Bull. Soc. chim.*, (2), 2, 83, 1864; J. A. Muller, *ib.*, (4), 1, 13, 61, 1907; C. Fahlberg, *Zeit. anal. Chem.*, 13, 379, 1874; L. Blum, *ib.*, 29, 271, 1890; 31, 60, 1892; E. Murmann, *ib.*, 45, 174, 1906; *Monats.*, 19, 404, 1898; L. L. de Koninck and E. Prost (*l.c.*); A. Renard, *Compt. rend.*, 67, 450, 1868; M. Pouget, *ib.*, 129, 45, 1899; W. G. Waring, *Journ. Amer. Chem. Soc.*, 26, 4, 1904; 29, 265, 1907; A. H. Low, *ib.*, 15, 550, 1893; 22, 198, 1900; W. H. Seaman, *ib.*, 29, 205, 1907; W. H. Keen, *ib.*, 30, 225, 1908; G. C. Stone, *ib.*, 17, 475, 1895; 30, 904, 1908; Reports on this subject, *ib.*, 29, 262, 1907; *Min. Eng. World*, 40, 55, 1914; *Chem. News*, 67, 5, 17, 1893; F. M. Lyte, *ib.*, 31, 222, 1875; W. H. Keen, *ib.*, 98, 201, 1908; R. W. Mahon, *Amer. Chem. Journ.*, 4, 53, 1882; H. S. Pattinson and G. C. Redpath, *Journ. Soc. Chem. Ind.*, 24, 228, 1905; E. Donath and G. Hattensauer, *Chem. Ztg.*, 14, 323, 1890; Report in *Chem. News*, 67, 5, 17, 1893; E. Rupp, *Archiv Pharm.*, 241, 331, 1903; *Chem. Ztg.*, 33, 3, 1909; C. Kirschnick, *ib.*, 31, 960, 1907; E. T. Henderson, *Proc. Australian Inst. Min. Eng.*, 195, 1913; F. R. von Bichowsky, *Journ. Washington Acad. Sci.*, 17, 141, 1917; J. H. Hastings, *Met. Chem. Eng.*, 36, 506, 1917; K. Voigt, *Zeit. angew. Chem.*, 24, 2195, 1911; 26, 47, 1913; D. J. Demorest, *Journ. Ind. Eng. Chem.*, 5, 302, 1913; I. M. Kolthoff and E. J. A. H. Verzyl, *Zeit. anorg. Chem.*, 132, 318, 1924; *Rec. Trav. chim.*, 43, 380, 389, 1924; I. M. Kolthoff, *ib.*, 41, 425, 1922; F. Müller, *Zeit. anorg. Chem.*, 128, 125, 1923; A. H. Low, *Technical Methods of Ore Analysis*, New York, 252, 1922; N. W. Lord and D. J. Demorest, *Metallurgical Analysis*, New York, 203, 1924; S. Urbasch, *Chem. Ztg.*, 46, 101, 125, 133, 138, 1922; E. Beyne, *Bull. Soc. chim.*, 33, 507, 1924; E. G. R. Ardagh and G. R. Bongard, *Ind. Eng. Chem.*, 16, 297, 1924; G. G. Reissaus, *Zeit. anal. Chem.*, 69, 450, 1926; R. Nakaseko, *Mem. Coll. Sci. Kyoto*, 11A, 95, 1928; N. Joassart and E. Leclerc, *Bull. Soc. chim. Belg.*, 39, 231, 1930; E. Brennecke, *Zeit. anal. Chem.*, 86, 175, 1931; B. Kamienski and K. Karczewski, *Roczniki Chem.*, 11, 577, 1931; B. Park, *Journ. Amer. Chem. Soc.*, 54, 180, 1932; F. C. Breyer, *Eighth Inter. Congr. Appl. Chem.*, 25, 7, 1912; W. B. Price *et al.*, *Journ. Ind. Eng. Chem.*, 7, 457, 1915; L. A. Congdon, A. B. Guss and F. A. Wintor, *Chem. News*, 131, 65, 81, 97, 113, 1925; A. Hecquet, *Ann. Chim. anal. Chim. appl.*, 15, 10, 1933; S. Saito, *Bull. Inst. Phys. Chem. Research* (Tokyo), 8, 921, 1929; *Sci. Papers*, *ib.*, 24, 226, 1934; P. L. Hibbard, *Ind. Eng. Chem. Anal. Ed.*, 6, 423, 1934.

which give insoluble or sparingly soluble ferrocyanides—cadmium, copper, antimony,[1] arsenic,[2] iron, aluminium, manganese,[3] nickel, cobalt, lead and magnesium—should also be absent. Some of these substances, however, produce no appreciable effect if only present in small quantities—*e.g.* aluminium and lead.[4]

The composition of the precipitate varies according as the solution is alkaline, neutral or acid; according as the solution is acid with acetic or hydrochloric acid; if the hydrochloric acid be in excess, the potassium ferrocyanide will be decomposed, forming a blue solution which spoils the work. This all shows that *uniform conditions are indispensable for accurate work.*

The end-point is not very sensitive in the presence of hydrochloric acid, but it is sharpened a little in presence of ammonium chloride. In consequence, it is necessary to deduct from the burette reading the amount of the standard ferrocyanide solution needed to give the brown coloration, with the uranium nitrate used as indicator, in excess of that actually required to convert all the zinc to ferrocyanide. Since uranium ferrocyanide is soluble in hydrochloric acid, this excess is dependent upon the amount of hydrochloric acid present. Hence it is necessary to work under certain definite conditions which experience has shown to be the best, and to determine the allowance to be made for the indicator.

Standardising the Potassium Ferrocyanide Solution.—Dissolve 34·60 grms. of crystalline potassium ferrocyanide—$K_4Fe(CN)_6 . 3H_2O$—in water,[5] and make the solution up to a litre—if not clear, filter.[6] 1 c.c. corresponds with 0·01 grm.

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[1] Cadmium salts are fatal to the success of the determination of zinc by the ferrocyanide process. Cadmium ferrocyanides—$Cd_2Fe(CN)_6$ and $K_2CdFe(CN)_6$, or a mixture of the two —are formed (E. H. Miller, *Journ. Amer. Chem. Soc.*, **22**, 541, 1900; **24**, 226, 1902; H. Weil, *Zeit. anal. Chem.*, **52**, 549, 1913). If cadmium, copper and antimony be present, a difficult separation by hydrogen sulphide may be necessary (I. M. Kolthoff and J. C. van Dijk, *Pharm. Weekblad*, **59**, 1351, 1922). It is generally considered best to precipitate the copper, lead, cadmium and antimony by boiling the dilute hydrochloric acid solution with a piece of metallic aluminium (page 309). Lead will precipitate copper in an acidified solution. If copper is to be precipitated with aluminium, ammonium salts should be absent. If much aluminium be present, derived from the solution of metallic aluminium, the results of the ferrocyanide titration will be irregular (E. H. Miller and E. J. Hall, *School Mines Quart.*, **21**, 270, 1900; *Chem. News*, **82**, 177, 1900).

[2] If arsenic be present, some iron may escape precipitation with ammonia. In that case, the solution may be evaporated to dryness. Boiling the residue with concentrated hydrochloric acid and bromine will expel the arsenic.

[3] M. Galleti (*Zeit. anal. Chem.*, **4**, 213, 1865) removes iron and manganese by shaking the solution with lead dioxide and filtering before titrating. K. Voigt (*Zeit. angew. Chem.*, **24**, 2195, 1911; **26**, 47, 1913) and J. W. Springer (*ib.*, **30**, 173, 1917) remove manganese by means of bromine (page 394) and copper by hydrogen sulphide. D. J. Demorest (*Journ. Ind. Eng. Chem.*, **5**, 302, 1913) says that ammonium carbonate separates zinc and copper from iron, aluminium, manganese, lead and cadmium, the zinc and copper remaining in solution. The copper is then precipitated as sulphide. A. Renard (*Bull. Soc. chim.*, (2), **11**, 473, 1869) removed manganese by sodium phosphate in ammoniacal solution; on analysis an untreated sample gave 1·036 grm. zinc and the same sample, after the above treatment, 0·998 grm. zinc. See also G. van Pelt, *Bull. Soc. chim. Belg.*, **28**, 101, 138, 1914; E. Seeligmann, *Zeit. anal. Chem.*, **53**, 594, 1914; **54**, 104, 1915. For the separation of zinc from aluminium and magnesium, see L. Harn and J. Dornauf, *Ber.*, **55B**, 3434, 1922; H. L. Piotrowski, *Przemysl Chem.*, **14**, 105, 1930.

[4] V. Lehner and C. C. Meloche (*Journ. Amer. Chem. Soc.*, **35**, 134, 1913), W. D. Treadwell and D. Chervet (*Helv. Chim. Acta*, **5**, 633, 1922) and J. M. Kolthoff (*Chem. Weekblad*, **24**, 203, 1927) show that lead does no harm in the ordinary ferrocyanide titration for zinc.

[5] L. Blum (*Zeit. anal. Chem.*, **34**, 285, 1895) deals with the impurities in commercial potassium ferrocyanide.

[6] F. Moldenhauer (*Chem. Ztg.*, **15**, 223, 1891; *Chem. News*, **64**, 150, 1891) proposes to prevent the decomposition of the solution by adding 1 to 2 grms. of potassium hydroxide per litre. The standard solution should be preserved in darkness.

of zinc oxide. In order to standardise this solution, ignite pure zinc oxide [1] and cool in a desiccator to ensure freedom from moisture and carbonates. Dissolve exactly 10 grms. in concentrated hydrochloric acid, add ammonia until a slight permanent precipitate is formed; dissolve this in a drop or two of dilute hydrochloric acid; add 6 c.c. of concentrated hydrochloric acid and 10 grms. of ammonium chloride and make the solution up to a litre. 1 c.c. corresponds with 0·01 grm. of ZnO.

The Titration.—Pipette 25 c.c. of the standard solution of zinc oxide into a 600 c.c. flask or beaker and sufficient water to make about 180–200 c.c. Warm the solution to about 70°-80°, and pour about half into another beaker. Add the standard ferrocyanide solution from a burette, 1 c.c. at a time, until the solution has a greyish colour and a drop in contact with a drop of uranium nitrate solution [2] on a porcelain plate (page 501) gives a distinct brown coloration. Mix the two solutions. Suppose that 14 c.c. of the ferrocyanide give no coloration with the first half and 15 c.c. give a distinct brown. Then at least 28 c.c. of ferrocyanide solution will be needed for the titration. Hence a total 28 c.c. of ferrocyanide may be added without fear of exceeding the limit. Then add the ferrocyanide drop by drop and test for the end by means of the spot test. Pour the solution backwards and forwards from one beaker to the other in finishing the titration. This procedure is less tedious than titrating the whole solution directly and there is less danger of exceeding the limit. A little time should be allowed for the spot test to change colour or the end-point may be exceeded. This may be corrected as follows:—Let the test drops be added in regular order and keep a memorandum of the corresponding burette readings. The first spot which shows the brown coloration after standing a short time is the proper reading. This gives the volume of the ferrocyanide solution corresponding with the zinc in the given solution. Hence the amount of zinc oxide is readily computed.[3] ·

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[1] Zinc oxide is preferable since it is more easily procured free from metallic impurities than is zinc itself.

[2] URANIUM NITRATE SOLUTION.—15 grms. of uranium nitrate in 100 c.c. of water (M. Galleti, *Zeit. anal. Chem.*, **4**, 213, 1865). H. Nissenson and W. Kettembeil (*Chem. Ztg.*, **29**, 591, 1905) and W. G. Waring (*Journ. Amer. Chem. Soc.*, **26**, 4, 1904) use a 1 per cent. solution of ammonium heptamolybdate instead of uranium nitrate or acetate, provided hydrogen sulphide is absent. A trace of hydrogen sulphide can be destroyed by a small crystal of sodium sulphite. F. Moldenhauer (*Chem. Ztg.*, **13**, 1220, 1889; **15**, 223, 1891; *Chem. News*, **64**, 150, 1891) draws a narrow streak of a 4 per cent. solution of copper sulphate along strips of white filter-paper by means of a camel-hair brush. The strips are dried quickly and preserved in stoppered bottles. When a drop of liquid containing potassium ferrocyanide is placed on the white portion of a strip, if free potassium ferrocyanide soaks into the portion containing copper sulphate a reddish mark is produced. For the use of iron salts as internal indicators, see S. Urbasch, *Chem. Ztg.*, **46**, 6–138, 1922; S. L. Robertson, *Journ. Roy. Tech. Coll. Met. Club, Glasgow*, (6), 37, 1928; J. Guéron, *Ann. Chim. anal. Chim. appl.*, **14**, 393, 1932. J. W. Springer (*Zeit. angew. Chem.*, (1), **30**, 173, 1917) uses ferrous chloride in aqueous acetic acid as an external indicator. L. Fernandes (*Giorn. Chim. Ind. Appl.*, **6**, 334, 1924), recommends alkali molybdates; W. H. Cone and L. C. Cady (*Journ. Amer. Chem. Soc.* **49**, 356, 1927), I. M. Kolthoff (*Chem. Weekblad*, **24**, 203, 1927), I. M. Kolthoff and E. A. Pearson (*Ind. Eng. Chem. Anal. Ed.*, **4**, 147, 1932) diphenylbenzidine or diphenylamine for internal use; no indicator allowance is needed with the former. E. J. Kocsis and L. Pollak (*Acta Lit. Sci. Univ. Hung. Fran. Joseph Sect. Chem. Min. Phys.*, **4**, 147, 1934), sodium alizarin sulphonate. I. Tananaev and M. Georgobiani (*Zeit. anal. Chem.*, **107**, 92, 1936) use methyl red as an adsorption indicator. G. C. Stone (*Journ. Amer. Chem. Soc.*, **17**, 473, 1895) recommends a dilute solution of cobalt nitrate as indicator and claims that it gives better results than uranium, copper or iron salts. Note that commercial "uranium acetate" may be either uranyl acetate or sodium uranyl acetate.

[3] There is a danger of under-titrating when the solution is cold, owing to the slow reaction between the ferrocyanide and the zinc. F. Schulz (*Chem. Ztg.*, **33**, 1187, 1909) places an open tube (12–15 mm. diameter) in the liquid to be titrated and then titrates as usual, while

Indicator Allowance.[1]—Pour 180 to 200 c.c. of water into a beaker, add 10 grms. of ammonium chloride and 6 c.c. of concentrated hydrochloric acid. Warm the mixture to 70°–80° and add ferrocyanide from the burette with constant stirring until a drop of the solution gives a distinct brown colour when applied to a spot of the uranium nitrate indicator on a white glazed tile. The volume needed should not be greater than 0·5 c.c., and, in subsequent titrations, it should be subtracted as a correction from each burette reading.[2]

Zinc can also be determined volumetrically by titration with a standard solution of sodium sulphide [3]—Schaffner's method. Opinion is divided as to the merits of the process; some maintain that the composition of the test solution must be carefully controlled, and others that such precautions are immaterial. The sodium sulphide solution must be checked frequently against a standard solution of zinc.

§ 188. The Evaluation of Zinc Oxide.

When the zinc oxide is to be determined in a commercial sample of the oxide, proceed as indicated in the preceding section for the preparation of the standard zinc oxide solution and keep the conditions as nearly the same as possible, *i.e.* titrate at 70°–80° in a volume of 180–200 c.c. of solution, containing 6 c.c. of concentrated hydrochloric acid [4] and 10 grms. of ammonium chloride. A little lead in the solution will not affect the result appreciably.

Zinc oxide is soluble, even after ignition, in a mixture of equal volumes of ammonia (sp. gr. 0·924), ammonium carbonate (20 per cent.) and ammonium chloride (20 per cent.). Hence Tambon [5] determines the zinc oxide in "zinc white" and "zinc grey" by digesting 10 grms. of the sample with 300 c.c. of the above solution and shaking the mixture a few minutes. After standing 10 minutes,[6] filter, wash and dry the insoluble residue. The difference between this weight and the original sample represents the zinc oxide. Instead of estimating the soluble zinc by difference, it can be determined volumetrically. If soluble zinc salts are present, they must be first removed by washing with warm water before digesting with Tambon's solution.[7]

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rotating the beaker, the liquid inside the tube not being acted upon. Hence, by using the tube as a stirrer, the untitrated liquid within it neutralises any over-titration. The last drops of the standard solution are then added very cautiously.

[1] An ingenious method for calculating the indicator allowance in this and other titrations is given by B. Park, *Ind. Eng. Chem. Anal. Ed.*, 8, 32, 1936.

[2] B. Park (*Journ. Amer. Chem. Soc.*, 54, 180, 1932) points out that, in the analysis of zinc ores, when hydrogen sulphide is added to precipitate any copper or to reduce oxidising agents in the zinc solution before titration, excess hydrogen sulphide will also reduce any ferricyanide in the standard ferrocyanide, thus altering its titre. Hence he standardises the ferrocyanide solution against a zinc standard in the presence of hydrogen sulphide.

[3] M. Schaffner, *Berg. Hütt. Ztg.*, 16, 40, 1857; *Journ. prakt. Chem.*, (1), 73, 410, 1858; C. Künzel, *ib.*, (1), 88, 486, 1863; S. Urbasch, *Chem. Ztg.*, 46, 101, 125, 133, 138, 1922; C. Boy, *ib.*, 47, 758, 1923; E. Donath and G. Hattensaur, *ib.*, 14, 323, 1890; A. Deckers, *Bull. Soc. chim. Belg.*, 20, 164, 1906; E. Beyne, *ib.*, 33, 507, 1924; 34, 38, 1925; V. Hassreidter, *ib.*, 20, 373, 1906; *Zeit. anal. Chem.*, 56, 311, 506, 1917; J. Patek, *ib.*, 55, 427, 1916; W. Orlik, *ib.*, 56, 141, 1917; G. Fenner and Rothschild, *ib.*, 56, 384, 1917; V. Hassreidter, *Zeit. angew. Chem.*, 21, 66, 1908.

[4] If more hydrochloric acid be used, the indicator allowance will be larger than 0·5 c.c. and the result will be uncertain.

[5] J. Tambon, *Bull. Soc. chim.*, (4), 1, 823, 1907.

[6] "Zinc grey" requires 30 minutes' digestion.

[7] Recent work on the determination of zinc is discussed by M. Frommes, *Zeit. anal. Chem.*, 97, 36, 1934. For the determination of small amounts of zinc by "dithizone," see P. L. Hibbard, *Ind. Eng. Chem. Anal. Ed.*, 9, 127, 1937, and footnote 6, page 372.

CHAPTER XXVIII.

THE DETERMINATION OF MANGANESE.

§ 189. The Effect of Manganese on Silicate Analyses.

FIRECLAYS often contain up to 0·2 per cent. of manganese. This element is usually ignored in clay analyses when, as Hillebrand[1] has shown, if present, it will be found distributed between the ammonia precipitate, the lime and the magnesia, even when a double ammonia precipitation is made. Much remains in the ammonia precipitate, presumably because the manganese is peroxidised, when it is precipitated in ammoniacal solutions.[2] For instance, Steiger found:—

Table L.—Distribution of Manganese among the Different Constituents of a Clay Analysis.

Composition of rock.			Manganese found.			
Al_2O_3 Fe_2O_3.	CaO.	MgO.	Total.	With Al_2O_3 Fe_2O_3 by diff.	With CaO.	With MgO.
9·35	11·84	2·81	0·311	0·036	0·023	0·252
12·71	11·98	4·30	0·442	0·088	0·016	0·338
4·80	50·51	1·04	0·700	0·301	0·087	0·312
3·49	3·99	0·92	0·016	0·016	nil	nil
1·00	28·04	19·11	0·574	0·032	0·101	0·441

If the manganese is to be determined in a silicate or clay, one of two methods may be adopted.[3] The manganese is either precipitated with the aluminium hydroxide by peroxidising the manganese as indicated on page 157; or the iron and aluminium hydroxides are precipitated by the basic acetate process, redissolved and reprecipitated by ammonia. The manganese will be found in the combined filtrates.[4] In the former case, the manganese can be deter-

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[1] W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **700**, 134, 1919; P. de Sorray, *Bull. Assoc. Chim. Sucr. Dist.*, **27**, 671, 1910; H. Rose, *Pogg. Ann.*, **110**, 292, 1860; *Chem. News*, **2**, 266, 1860; L. A. Dean and E. Truog, *Ind. Eng. Chem. Anal. Ed.*, **7**, 383, 1935. G. E. F. Lundell and H. B. Knowles (*Journ. Amer. Chem. Soc.*, **45**, 676, 1923) state that moderate amounts of iron and aluminium can be separated from manganese and nickel by precipitation with ammonia just as well as by any other process. Compare E. A. Ostroumov, *Zavodskaya Lab.*, **6**, 16, 1937.

[2] See footnote 5, page 383.

[3] Many other methods are available. See A. R. Taborda, *Rev. Brasil Chim.* (São Paulo), **3**, 158, 1937.

[4] When minute amounts of manganese are in question, it may be well to bear in mind that laboratory glass generally contains a little manganese, which is dissolved out by alkali— R. A. Gortner, *Amer. Chem. Journ.*, **39**, 157, 1908.

mined by the colorimetric process in an aliquot portion of the pyrosulphate fusion. In the latter case, the manganese can be precipitated by ammonium sulphide, or by bromine, and subsequently determined colorimetrically, or gravimetrically as phosphate. The basic acetate process is generally used for the separation of alumina and iron from manganese, zinc, cobalt and nickel.

§ 190. The Detection of Manganese.

Sacher [1] detects one part of manganese in 200,000 parts of solution by precipitating manganous hydroxide by alkali, allowing the precipitate to oxidise partially in air and then treating with a few drops of 0·5N-oxalic acid until *just* dissolved. A red coloration is developed sharply. Reducing agents, tannic acid, excess of oxalic acid and high temperatures should be avoided.

Leitmeier [2] detects manganese in rocks by adding to a spot of the solution of the mineral on filter-paper a drop of aqueous potash, followed by a drop of a solution of benzidine in acetic acid. A blue colour appears if manganese is present.

§ 191. The Precipitation of Manganese by the Bromine Process.

Add 15 c.c. of 33 per cent. sodium acetate solution to the filtrates from, say, the basic acetate separation, and then add 2–3 c.c. of liquid bromine.[3] Heat the solution to boiling. If the solution, on standing, has a yellow colour, sufficient bromine is present; if not, add more bromine. Filter off the precipitate on a close-grained filter-paper. Add more bromine to the filtrate and boil again. If more manganese is thrown down, filter and repeat the process until no manganese is precipitated. Wash the precipitate.[4] If the later washings carry any manganese, re-filter.

The mixed precipitates are now ignited and weighed as Mn_3O_4.[5] This

[1] J. F. Sacher, *Chem. Ztg.*, **39**, 319, 1915; *Chem. Zentr.*, (1), 438, 1916. For modifications of this test, see W. Prandtl, *Ber.*, **49**, 1613, 1916; V. Macri, *Boll. chim. farm.*, **56**, 377, 1917; H. Caron and D. Raquet, *Ann. Chim. anal.*, (2), **1**, 174, 1919; G. Denigès, *ib.*, (2), **2**, 215, 1920.

[2] H. Leitmeier, *Tsch. Min. Petr. Mag.*, **41**, 87, 1931.

[3] Liquid bromine is recommended because it keeps down the volume of the solution. Some add bromine water, that is, water saturated with bromine. The latter is made by keeping water in a bottle with an excess of liquid bromine. L. L. de Koninck (*Zeit. anal. Chem.*, **18**, 468, 1879; *Chem. News*, **43**, 34, 1881) recommends a saturated solution of bromine in a 10 per cent. aqueous solution of potassium bromide. Others recommend a saturated solution of bromine in concentrated hydrochloric acid. The latter solution is strongly acid; Koninck's solution is neutral. For the presence of bromoform in commercial bromine, see S. Reymann, *Ber.*, **8**, 792, 1875; G. Torossian, *Journ. Ind. Eng. Chem.*, **8**, 663, 1916; R. Namias, *L'Ind. chim. min. met.*, **4**, 52, 1917.

[4] It is very difficult to wash the precipitate free from the alkalies carried down by the manganese oxide. Ammonium acetate in place of sodium acetate in the basic acetate separation helps a little, but the separation of manganese is not so good. A. G. M'Kenna, *Tech. Quart.*, **3**, 333, 1890; *Chem. News*, **63**, 184, 1891; V. Eggertz, *ib.*, **18**, 232, 1868; *ib.*, **43**, 226, 1881; C. Reinhardt, *Chem. Ztg.*, **10**, 323, 357, 372, 1886; C. Holthof, *Zeit. anal. Chem.*, **23**, 491, 1884; F. Kessler, *ib.*, **18**, 1, 1879; N. Wolff, *ib.*, **22**, 520, 1883; P. Waage, *ib.*, **10**, 206, 1871; H. Kämmerer, *Ber.*, **4**, 218, 1871.

[5] S. U. Pickering, *Chem. News*, **43**, 225, 1881; C. R. A. Wright and A. P. Luff, *Journ. Chem. Soc.*, **33**, 525, 1878; C. R. A. Wright and A. E. Menke, *ib.*, **37**, 775, 1880; W. Dittmar, *ib.*, **17**, 294, 1864; J. and H. S. Pattinson, *Journ. Soc. Chem. Ind.*, **10**, 333, 1891; E. H. Saniter, *ib.*, **13**, 112, 1894; H. D. Richmond, *Analyst*, **19**, 99, 1894; F. A. Gooch and M. Austin, *Zeit. anorg. Chem.*, **17**, 268, 1898; R. Schneider, *Pogg. Ann.*, **107**, 605, 1869; C. Meineke, *Zeit. angew. Chem.*, **1**, 3, 1888; W. C. Heraeus and W. Geibel, *ib.*, **20**, 1892, 1907; A. Gorgeu, *Compt. rend.*, **106**, 743, 1888; W. W. Randall, *Amer. Chem. Journ.*, **19**, 682, 1897; St C. Deville, *Compt. rend.*, **56**, 977, 1863; *Chem. News*, **7**, 294, 1863; Ballot, *Bull. Sci. pharmacol.*, **26**, 514, 1919; *Chem. Zentr.*, (2), 425, 1920; W. Cornelius, *Pharm. Ztg.*, **58**, 427, 1913; M. Herschkowitsch, *Zeit. anal. Chem.*, **59**, 11, 1920.

weight multiplied by 0·93008 gives the corresponding amount of MnO. If the crucible be surrounded by oxidising gases during the ignition, the composition of the precipitate will not deviate appreciably from Mn_3O_4; but if reducing gases be present, this formula will not represent the composition of the ignited precipitate (page 166). MnO is formed if the manganese compound be calcined at a red heat in a Rose's crucible (fig. 98) in a vigorous current of hydrogen; and the higher oxides form Mn_3O_4 if ignited in a current of carbon dioxide, or the sesquioxide, Mn_2O_3, by ignition in a current of oxygen.[1] The MnO formed as just described is said to be a "convenient and accurate form in which to weigh manganese."

The chief disadvantages of the bromine precipitation are: (1) the contamination of the precipitate with alkalies; and (2) uncertainty in the composition of the ignited oxide. A reprecipitation by bromine and ammonia will generally free the precipitate from foreign contaminations. Instead of weighing the precipitate as Mn_3O_4, many prefer to dissolve the moist precipitate in dilute acid and determine the manganese volumetrically, colorimetrically or gravimetrically by the phosphate process.

Other oxidising agents—ammonium, potassium or sodium persulphate,[2] hydrogen peroxide[3]—are often used instead of bromine for precipitating manganese as hydrated peroxide.[4]

§ 192. The Precipitation of Manganese by Ammonium Sulphide.

Ammonium sulphide alone precipitates manganese, zinc, nickel and cobalt sulphides very imperfectly; but if ammonium chloride be present, precipitation is practically complete. Fresenius [5] says that these elements can be pre-

[1] P. N. Raikow and P. Tischkoff, *Chem. Ztg.*, **35**, 1013, 1911.

[2] L. Dede, *Chem. Ztg.*, **35**, 1077, 1911; G. van Pelt, *Bull. Soc. chim. Belg.*, **28**, 101, 138, 1914; M. Huybrechts and N. Joassart, *ib.*, **27**, 130, 1913; M. Herschkowitsch, *Zeit. anal. Chem.*, **59**, 11, 1920; K. A. Jensen, *ib.*, **86**, 422, 1931; M. Dittrich and C. Hassel, *Ber.*, **36**, 284, 1423, 1903; **35**, 3266, 1902. If cobalt be present, along with manganese salts, some cobalt will be precipitated by the persulphate, as well as manganese peroxide. F. Mawrow, *Zeit. anorg. Chem.*, **24**, 263, 1900; T. Somiya, *Journ. Soc. Chem. Ind. Japan*, **33**, 255B, 1930. Compare G. E. F. Lundell, *Journ. Amer. Chem. Soc.*, **45**, 2600, 1923; H. W. Willard and J. J. Thompson, *Ind. Eng. Chem. Anal. Ed.*, **3**, 399, 1931.

[3] P. Jannasch, *Prakt. Leitfaden Gewichtsanalyse*, Leipzig, 47, 1897; P. Jannasch and H. Lehnert, *Zeit. anorg. Chem.*, **12**, 134, 1896; P. Jannasch and E. von Cloedt, *ib.*, **10**, 399, 405, 1895; P. Jannasch and R. Niederhofheim, *Ber.*, **24**, 3945, 1891; P. Jannasch and J. F. MacGregory, *Journ. prakt. Chem.*, (2), **43**, 402, 1891; A. J. Walker and W. Farmer, *Proc. Chem. Soc.*, **30**, 139, 1914; A. Carnot, *Compt. rend.*, **116**, 1295, 1893; *Bull. Soc. chim.*, (3), **9**, 613, 1893; G. Lunge, *Ber.*, **18**, 1874, 1885; *Compt. rend.*, **116**, 1375, 1893; H. C. Jones, *ib.*, **117**, 781, 1893; *Amer. Chem. Journ.*, **12**, 279, 1890; G. van Pelt, *Bull. Soc. chim. Belg.*, **28**, 101, 138, 1914; I. S. Teletov and N. N. Andronikova, *Bull. Soc. chim.*, (4) **45**, 674, 1929; *Ukrain Chem. Journ.*, **4**, 341, 1929; H. J. Taverne, *Chem. Weekblad*, **20**, 210, 1923.

[4] M. Dittrich and C. Hassel, *Ber.*, **36**, 284, 1423, 1903; *Zeit. anal. Chem.*, **43**, 382, 1904; M. Dittrich, *Ber.*, **35**, 4072, 1902; M. E. Pozzi-Escot, *Ann. Chim. anal.*, **7**, 376, 1902; H. Baubigny, *Compt. rend.*, **135**, 965, 1110, 1902; **136**, 449, 1325, 1903; G. von Knorre, *Zeit. angew. Chem.*, **14**, 1149, 1901; **16**, 905, 1903; *Zeit. anal. Chem.*, **43**, 1, 1904; **44**, 88, 1905; E. Donath, *ib.*, **44**, 698, 1905; H. Lüdert, *Zeit. angew. Chem.*, **17**, 422, 1904; H. P. Smith, *Chem. News*, **90**, 237, 1904; H. Rubricus, *Stahl Eisen*, **25**, 890, 1905; M. Marqueyrol and L. Toquet, *Ann. Chim. anal. Chim. appl.*, (2), **9**, 289, 324, 1927; E. V. Holt and H. F. Harwood, *Min. Mag.*, **21**, 318, 1927.

[5] R. Fresenius, *Journ. prakt. Chem.*, (1), **82**, 265, 1861; *Zeit. anal. Chem.*, **11**, 419, 1872; H. Raab and L. Wessely, *ib.*, **42**, 433, 1903; A. Classen, *ib.*, **16**, 319, 1877; **8**, 370, 1869; C. Meineke, *Zeit. angew. Chem.*, **1**, 3, 1888; A. Völker, *Liebig's Ann.*, **59**, 38, 1846; P. de Cleremont and H. Guiot, *Bull. Soc. chim.*, (2), **27**, 353, 1877; J. C. Olsen and W. S. Rapalje, *Journ. Amer. Chem. Soc.*, **26**, 1615, 1904; J. C. Olsen, E. S. Clowes and W. O. Weidmann,

cipitated from solutions containing the equivalent of $\frac{1}{100,000}$ of manganese oxide, and $\frac{1}{500,000}$ of nickel or cobalt oxide in presence of an excess of ammonium chloride.[1] If free ammonia be present, the precipitation of manganese and nickel sulphides is retarded and a certain amount of these elements remains in solution.

There are at least two varieties of manganese sulphide.[2] The one is pink or flesh-coloured and colloidal and readily passes through the filter-paper. Nor does the pink variety settle readily from the solution. The other sulphide is green in colour, coarse grained, crystalline and settles quickly. The latter can be easily filtered and washed. The pink variety, in presence of an excess of ammonium sulphide,[3] soon passes into the green variety when heated, but the change is retarded by the presence of ammonium chloride and many foreign salts.[4] Hence ammonium chloride facilitates the separation of manganese sulphide, but hinders the transformation of the pink into the green sulphide. The pink modification is the first product of the reaction and this is transformed into the green modification later on. The analyst must there-fore use methods which ensure a complete conversion of the manganese into sulphide and the transformation of the pink into the green sulphide. The best conditions are: (1) an excess of ammonium chloride before adding the sulphide; and (2) a large excess of ammonium sulphide in hot solutions. The ammonium sulphide must be free from yellow polysulphide, since manganese sulphide is slightly soluble in ammonium polysulphide.[5]

Suppose, then, that the manganese is to be precipitated by ammonium sulphide. Evaporate the filtrate, if necessary, to about 200 c.c. Pour the solution into an Erlenmeyer's flask; add 2-3 grms. of ammonium chloride and ammonia until the solution is alkaline. Pass hydrogen sulphide through the boiling solution [6] for about 10 minutes. Cork the flask and let it stand for about 24 hours in a warm place.[7] This procedure gives

ib., **26**, 1622, 1904; F. Muck, *Zeit. Chem.*, (2), **5**, 580, 1869; (2), **6**, 6, 1870; H. How, *Chem. News*, **19**, 137, 1870; W. Böttger, *Ber.*, **33**, 1019, 1900; *Chem. News*, **82**, 247, 1900; M. Antony and P. Donnini, *Gazz. Chim. Ital.*, **23**, i, 560, 1893; F. Seeligmann, *Zeit. anal. Chem.*, **53**, 594, 1914; **54**, 104, 1915.

[1] And $\frac{1}{500,000}$ of zinc oxide, if zinc be present.

[2] V. M. Fischer, *Journ. Russ. Phys. Chem. Soc.*, **46**, 1481, 1519, 1914.

[3] Not with sodium or potassium sulphide (Muck, *l.c.*).

[4] A. Villiers, *Compt. rend.*, **159**, 67, 1914.

[5] For the retarding action of salts of organic acids on the precipitation of manganese sulphide, see page 384; and for the retarding action of ammonium salts, see H. Rose, *Chem. News*, **2**, 302, 1860.

[6] Fischer (*l.c.*) says that if the solution be boiled, alkaline earth metals may be precipitated as carbonates, due to absorption of carbon dioxide from the air. He recommends the follow-ing procedure: To 100-200 c.c. of solution add 5-15 grms. of ammonium chloride and 50-60 c.c. of ammonia (sp. gr. 0·895). Now from a dropping funnel add, in the course of 10-15 minutes, 50-60 c.c. of ammonium hydrosulphide, freshly prepared from 2·5 per cent. ammonia solution. Shake constantly during the addition but do not warm. If the sulphide is not entirely in the green form at the end of the addition, cork the flask and stand for 15-90 minutes. Dilute to 500-700 c.c. with cold, freshly boiled distilled water, filter and wash with a dilute solution of the precipitant, containing a little ammonium chloride. E. Murmann (*Monats.* **19**, 404, 1898) adds a little mercuric chloride before passing the hydrogen sulphide through the hot solution. The precipitate of the green sulphide so obtained is easily filtered and washed. The mercury volatilises as soon as the precipitate is ignited. Seeligmann (*l.c.*) adds a little hydrogen peroxide to the solution before adding ammonia.

[7] If the solution happens to contain much lime, as sometimes occurs in the analysis of blast-furnace slags, the prolonged standing leads to the formation of crystals, probably calcium thiosulphate (L. Blum, *Zeit. anal. Chem.*, **28**, 454, 1889). In that case, it is better to follow H. Rose (*Ausführliches Handbuch der analytischen Chemie*, Braunschweig, **1**, 167, 1864) and boil the solution while repeatedly adding ammonium sulphide. Filter at once. No calcium thiosulphate is then formed.

a granular precipitate.[1] Collect the precipitate [2] on a small filter-paper—say 7·5 cm. diameter. Wash with water containing a little colourless ammonium sulphide.[3] Dissolve the precipitate in a little dilute sulphuric acid if the manganese is to be determined gravimetrically as phosphate.

§ 193. The Gravimetric Determination of Manganese— Gibbs' Phosphate Process.

Manganese is separated from the alkaline earths by precipitation with ammonium sulphide, or with oxidising agents like potassium chlorate, potassium persulphate or bromine. The precipitate is dissolved in hydrochloric acid (1 : 1), and microcosmic salt is added to the solution. A precipitate of ammonium manganese phosphate is obtained similar to the precipitate obtained with magnesium.[4] This is converted into the pyrophosphate by ignition and then weighed.

First Precipitation.—The cold solution of the manganese oxide in hydrochloric acid (1 : 1) is supposed to contain no more manganese than is represented by 0·1 grm. MnO per 100 c.c. of solution. Add an excess of a cold saturated solution of microcosmic salt [5] with constant stirring. Then add a few grms. of ammonium chloride, followed by a slight excess of dilute ammonia. Heat the mixture until the precipitate becomes crystalline, and let the whole stand for about 1½ hours, till cold. Filter and wash with cold, slightly ammoniacal water,[6] dry the precipitate at a gentle heat and ignite as described below. If the manganese salt is associated with other salts in solution, a second precipitation must be made.[7] A large excess of microcosmic salt is necessary in order to

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[1] A black precipitate indicates that nickel, cobalt, copper or platinum may be present. With clays, however, there is little chance of this, but platinum may be derived from the platinum crucible during the pyrosulphate fusions. For the separation when zinc, etc., is present, see page 385.

[2] If some sulphide sticks to the walls of the flask or beaker, wash the vessel with dilute nitric acid. The resulting solution is either added to that obtained by dissolving the precipitate, or it is evaporated to dryness in a weighed crucible, calcined to Mn_3O_4, and the result added to the weight of the main precipitate. It is important to test the filtrate for manganese, and to test the precipitate for silica, barium, etc., if only one precipitation followed by roasting to Mn_3O_4 be made—J. and H. S. Pattinson, *Chem. News*, 81, 193, 1900.

[3] L. Blum (*Zeit. anal. Chem.*, 44, 7, 1905) says there is frequently a slight oxidation of sulphide to sulphate, and in consequence traces of barium and strontium, if present, may be precipitated.

[4] W. Gibbs, *Chem. News*, 17, 195, 1868; *Amer. J. Science*, (2), 44, 216, 1867; *Zeit. anal. Chem.*, 7, 101, 1868; R. Fresenius, *ib.*, 11, 415, 1872; F. Kessler, *ib.*, 18, 8, 1879; H. D. Dakin, *ib.*, 39, 784, 1900; *Chem. News*, 83, 37, 1901; W. Böttger, *ib.*, 82, 101, 1900; *Ber.*, 33, 1019, 1900; A. G. M'Kenna, *Tech. Quart.*, 3, 333, 1890; *Chem. News*, 63, 184, 1891; T. Moore, *ib.*, 63, 66, 1891; G. L. Norris, *Journ. Soc. Chem. Ind.*, 20, 551, 1901; E. H. Saniter, *ib.*, 13, 112, 1894; R. C. Boyd, *School Mines Quart.*, 11, 355, 1890; L. Rürup, *Chem. Ztg.*, 20, 285, 337, 1896; A. Ledebur, *ib.*, 8, 910, 927, 963, 1884; F. A. Gooch and M. Austin, *Zeit. anorg. Chem.*, 18, 339, 1898; *Amer. J. Science*, (4), 6, 233, 1898; *Chem. News*, 78, 239, 246, 1898; C. E. Munroe, *Amer. Chem.*, 7, 287, 1877; M. Lindeman and J. Motteu, *Bull. Soc. chim.*, (3) 13, 523, 1895; F. H. Campbell, *Journ. Soc. Chem. Ind.*, 32, 3, 1912; L. W. Winkler, *Zeit. angew. Chem.*, 35, 234, 1922; R. Strebinger and J. Pollak, *Mikrochem.*, 4, 15, 1926; P. Nuka, *Zeit. anal. Chem.*, 87, 7, 1931; *Latvij Univ. Raksti*, 2, 1, 1931.

[5] AMMONIUM SODIUM PHOSPHATE SOLUTION.—A saturated solution has nearly 170 grms. per litre. 1·5 grms. suffice for 0·1 grm. of MnO. Hence 9 c.c. will be required per 0·1 grm. MnO.

[6] P. Nuka (*l.c.*) says that the only satisfactory wash liquor is a hot 1 per cent. solution of diammonium hydrogen phosphate, $(NH_4)_2HPO_4$; the latter is then washed away with 60 per cent. alcohol.

[7] D. Balarev and N. Desev (*Zeit. anal. Chem.*, 70, 444, 1927) say that the presence of much acetate, sulphate, potassium or sodium leads to high results and that the error caused by sodium acetate cannot be eliminated by reprecipitation.

render the precipitate insoluble, especially in the presence of ammonium salts.[1]

Second Precipitation.—Redissolve the precipitate in an excess of hydrochloric acid. Heat the solution to boiling and add a slight excess of ammonia and microcosmic salt solution. The flocculent white gelatinous precipitate of manganese ammonium phosphate so produced passes into a flesh-coloured crystalline precipitate—NH_4MnPO_4—when the solution is boiled, or allowed to stand for some time.[2] The precipitation is best performed in a platinum vessel; but a glass vessel is quite satisfactory. When cold, filter either through an asbestos-packed Gooch crucible or through filter-paper, and wash with very dilute, cold ammonia solution until the wash-water acidified with nitric acid gives no turbidity with a drop of silver nitrate solution. This is important.[3] Add more microcosmic salt to the filtrate. If a precipitate settles after standing several hours, filter it through a small filter-paper. Dry the precipitates.

Ignition of the Precipitate.—If the filtration has been done through filter-paper, transfer the dried precipitate to a watch-glass. Ignite the paper separately in a porcelain crucible. Then transfer the precipitate from the watch-glass and ignite at a red heat. The temperature should be raised very gradually, in order to prevent any solid from being carried away with the ammoniacal vapours. The ignited precipitate should be white or pale pink.

Calculation.—The weight of the calcined manganese pyrophosphate—$Mn_2P_2O_7$,—multiplied by 0·5 (or, more exactly, by 0·4998), and divided by the weight of the sample, represents the amount of manganese oxide—MnO—in the given sample.

Errors.—If the precipitate be coloured brown, the manganese was not all converted into the phosphate. In that case, redissolve the precipitate in hydrochloric acid (1 : 1), and repeat the precipitation with more microcosmic salt. If the precipitate is not all soluble in the hydrochloric acid, some silica was probably precipitated with the manganese. In that case, filter the solution, wash, ignite and weigh the insoluble silica. Deduct the weight of the silica from the weight of the nominal manganese phosphate.

The process does not give good results in the presence of zinc, nickel, copper and other metals which give precipitates of sparingly soluble phosphates in ammoniacal solutions. It is an excellent method for converting precipitates by, say, bromine into a weighable form, and for separating manganese from those elements which are not liable to precipitation in ammoniacal phosphate solutions.

In test experiments, using 50 c.c. of a saturated solution of microcosmic salt, 20 grms. of ammonium chloride and a solution diluted to 200 c.c., Gooch and Austin obtained the following figures:—

MnO used	.	0·0942	0·0942	0·0942	0·1885	0·1885	0·1885 grm.
MnO found	.	0·0951	0·0955	0·0956	0·1888	0·1886	0·1889 grm.
Error	.	0·0009	0·0013	0·0014	0·0003	0·0001	0·0004 grm.

[1] The proportion of ammonium chloride to the ammonium manganese phosphate should be as 50 : 1. A very large excess of ammonium chloride may be added without any perceptible solvent action. R. Fresenius (*l.c.*) says that 1 part of the precipitate dissolves in 32,092 parts of cold water, in 20,122 parts of boiling water, and in 1775 parts of a solution of ammonium chloride (1 : 70). This latter statement, however, does not hold good when an excess of the phosphate used for precipitating is present.

[2] A large excess of ammonium chloride favours a rapid transformation; ammonium nitrate is not so good.

[3] Ammonium chloride would be volatilised during the ignition, but a trace of manganese chloride might be formed. There is no danger from this if the washing be conducted as described in the text.

The positive error here observed appears to be due to the slight adsorption of the microcosmic salt by the precipitated phosphate.[1] The average error in duplicate determinations did not, therefore, exceed 0·001 grm. when expressed in terms of MnO.

§ 194. The Volumetric Determination of Manganese— Pattinson's Process.

A large number of rapid methods has been suggested, by precipitating the manganese as hydrated manganese dioxide—possibly $MnO(OH)_2$— by reagents such as potassium chlorate,[2] zinc oxide and bromine,[3] bleaching powder and ferric chloride,[4] ammonium persulphate,[5] and subsequently determining the manganese dioxide by one of the many available volumetric processes. These processes can be made to give accurate results under special conditions, but there is some uncertainty as to the composition of the precipitate, and in routine work an allowance is frequently made for the deviation in the composition of the precipitate from the assumed $MnO(OH)_2$. When ores are only occasionally analysed, the corrections are troublesome. Ledebur, Saniter, Rürup and others have examined Volhard's, Pattinson's and other methods. Pattinson's gives excellent results. This process is based on the fact that the whole of the manganese in a solution of manganese chloride can be precipitated as manganese dioxide in the presence of ferric or zinc chloride by an excess of an aqueous solution of calcium hypochlorite or bromine water.

Dissolution of the Mineral.—Digest 10 grms. of the finely powdered and dried (110°) mineral in 100 c.c. of concentrated hydrochloric acid. Add 5 c.c. of concentrated nitric acid and evaporate down to a small volume.[6] Transfer the solution to a 100 c.c. flask and make up to the mark with water.

Conversion of the Manganese Chloride into Manganese Peroxide.—Agitate the contents of the flask, and pipette 20 c.c. into a litre beaker or Erlenmeyer's flask. Add sufficient ferric chloride to make the amount of ferric and manganese chlorides present in the solution approximately equal. This ensures

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[1] The positive error introduced by precipitation in the presence of sodium salts has been pointed out by Balarev and Desev, Nuka and Winkler (see footnotes 6, 7, page 397). To avoid the introduction of sodium compounds, Winkler precipitates in boiling, faintly acid solution with a 20 per cent. solution of diammonium hydrogen phosphate. Nuka states that high and variable results are also obtained if the precipitate is made to become crystalline by heating; it should form slowly and be crystalline from the start.

[2] W. Hampe and M. Ukena, *Zeit. anal. Chem.*, **24**, 431, 1885; **32**, 369, 1893; A. P. Ford, *Trans. Amer. Inst. Min. Eng.*, **9**, 397, 1880; F. Williams, *ib.*, **10**, 100, 1881; R. Bolling, *Journ. Amer. Chem. Soc.*, **23**, 493, 1901; J. B. Hannay, *Journ. Chem. Soc.*, **33**, 269, 1878; F. F. Beilstein and L. Jawein, *Ber.*, **12**, 1586, 1879; M. A. von Reis, *Chem. Ztg.*, **15**, 1791, 1891; W. Hampe, *ib.*, **15**, 1579, 1891; F. A. Gooch and M. Austin, *Zeit. anorg. Chem.*, **17**, 253, 1898; M. Marqueyrol and L. Toquet, *Ann. Chim. anal. Chim. appl.*, (2), **9**, 289, 324, 1927.

[3] A. H. Low, *Journ. Anal. App. Chem.*, **6**, 663, 1892; *Chem. News*, **67**, 162, 1893.

[4] J. Pattinson, *Journ. Chem. Soc.*, **35**, 365, 1879; *Journ. Soc. Chem. Ind.*, **5**, 422, 1886; J. and H. S. Pattinson, *ib.*, **10**, 333, 1891; R. W. Atkinson, *ib.*, **5**, 365, 1886; E. H. Saniter, *ib.*, **13**, 112, 1894; J. Pattinson, *Chem. News*, **21**, 267, 1870; **41**, 179, 1880; G. Lunge, *ib.*, **41**, 78, 120, 141, 179, 181, 1880; W. Weldon, **41**, 207, 1880; C. R. A. Wright, *Journ. Chem. Soc.*, **37**, 22, 49, 1880; A. Ledebur, *Chem. Ztg.*, **8**, 910, 927, 963, 1884; F. Jean, *Bull. Soc. chim.*, (3), **9**, 248, 1893.

[5] G. von Knorre, *Zeit. angew. Chem.*, **14**, 1149, 1901; **16**, 905, 1903; P. Nicolardot, A. Réglade and M. Geloso, *Compt. rend.*, **170**, 808, 1920; *Ann. Chim. anal. Chim. appl.*, (2), **4**, 69, 102, 1922; J. Majdel, *Zeit. anal. Chem.*, **81**, 14, 1930; N. S. Krupenko, *Zavodskaya Lab.*, **3**, 268, 1934.

[6] The insoluble residue may be filtered off, ignited and fused with sodium carbonate. If the melt be coloured greenish-blue, take it up in dilute hydrochloric acid and add the solution to the main solution.

the precipitation of manganese dioxide instead of some lower oxide. Then add granular precipitated calcium carbonate, in small quantities at a time, until the free acid is neutralised and the solution, though clear, has a reddish-brown tinge. Now add 30 c.c. of a solution of zinc chloride [1] and 50 c.c. of a solution [2] of "chloride of lime" (or 25 c.c. of a saturated aqueous solution of bromine). Add more calcium carbonate, with constant stirring, until the latter remains undissolved. Now stir in 700 c.c. of hot water at about 70°. The supernatant liquid should be colourless. If it be pink (calcium permanganate), add 2 c.c. of methyl alcohol and boil; if it still be pink, repeat the treatment with methyl alcohol. Let the precipitate settle. Decant the clear supernatant liquid through an asbestos-packed Gooch crucible.[3] Wash four times by decantation with 300 c.c. of hot water (70°). Transfer the precipitate to the Gooch crucible without attempting to remove the last portions of the precipitate from the sides of the beaker. Wash the precipitate with hot (70°) water until the filtrate gives no blue coloration with starch-iodide paper.

The Titration.—The precipitate and the asbestos are placed in the original beaker. Dissolve the precipitate in dilute sulphuric acid (1 : 1). When the brown colour has disappeared,[4] add 50 c.c. of a freshly standardised solution of ferrous sulphate [5] acidified with sulphuric acid. Mix the solution thoroughly, and then titrate the excess of ferrous sulphate [6] with $0.1N$-potassium dichromate or potassium permanganate solution.[7]

Calculations.—Ten grms. of the ore were dissolved to give 100 c.c. of solution, and 20 c.c., equivalent to 2 grms. of the ore, were taken. 50 c.c. of ferrous ammonium sulphate solution, representing 89.24 c.c. of $0.1N$-dichromate, were added; but only 38.4 c.c. of the dichromate solution were required in the titration. Hence 2 grms. of the ore represented 50.84 c.c. of the dichromate solution. But 1 c.c. of $0.1N$-dichromate solution represents 0.004347 grm. of MnO_2 (or 0.003547 grm. MnO); hence, 50.84 c.c. of the dichromate solution represent 0.2210 grm. MnO_2 (or 0.1803 grm. MnO). That is, 2 grms. of the ore has the equivalent of 0.2210 grm. MnO_2 (or 0.1803 grm. MnO); that is, 11.05 per cent. of MnO_2 (or 9.02 per cent. MnO).

Errors.—This method will give results within 0.1 per cent. of the true percentage of manganese in a given sample. Lead, copper, nickel, cobalt and chromium lead to high results. The interference of up to 1 per cent. of lead,

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[1] Containing the equivalent of half a gram of metallic zinc per 30 c.c. If ferric chloride be used in place of zinc chloride, an error amounting to 0.4-0.5 per cent. of manganese may be introduced into the determination owing to the presence of manganese in this salt. To correct, the amount of manganese in the ferric chloride can be determined by boiling the solution with ammonia and a little hydrogen peroxide, dissolving the washed precipitate in sulphuric acid and a little sulphurous acid, and determining the manganese by the colorimetric process.

[2] Mix 15 grms. of fresh bleaching powder with 100 c.c. of water, and, after standing some time to settle, decant the clear liquid.

[3] The asbestos should be tested by a blank experiment with ferrous sulphate to make sure that it contains nothing which will reduce the manganese dioxide. G. W. Sargent and J. K. Faust (*Journ. Amer. Chem. Soc.*, **21**, 287, 1899) use a filter tube packed first with glass-wool, then with sand and finally with asbestos.

[4] If the ore contains organic matter, this must be filtered off through a Gooch crucible before attempting to oxidise the ferrous salt, since organic matter will reduce the ferric salts and give a high result.

[5] Containing the equivalent of about 10 grms. of metallic iron per litre; *i.e.* 70 grms. of ferrous ammonium sulphate per litre.

[6] A. Terreil, *Bull. Soc. chim.*, (2), **35**, 551, 1881.

[7] In any case the dichromate or permanganate should be standardised in a blank titration, using an amount of zinc or ferric chloride equal to that taken in the determination.

copper and nickel is not serious, but cobalt and chromium spoil the results. Higher oxides of these elements are probably precipitated with the manganese dioxide and, later on, oxidise the ferrous sulphate. For instance, 100 parts of Mn_3O_4, with 1 part of the metals indicated, gave the following results:

Lead.	Copper.	Nickel.	Cobalt.	Chromium.
100·23	100·23	100·23	100·64	100·60 per cent.

In the absence of these disturbing elements, $100\pm0\cdot1$ per cent. would have been obtained.

§ 195. The Volumetric Determination of Manganese— Volhard's Process.

Guyard [1] has shown that if a feebly acid or neutral solution of manganese sulphate or nitrate be treated with a solution of potassium permanganate, a compact dark brown precipitate of a manganic acid is formed, which is sometimes said to be H_2MnO_3. The permanganate is decolorised as long as any manganese salt remains in solution; any further addition of the permanganate produces a pink coloration. In reality, the manganic acid $MnO(OH)_2$ is not precipitated, but rather a manganese manganite the composition of which varies with the conditions of the experiment. It is accordingly difficult to get uniformly good results with Guyard's process. The reaction has been the subject of many investigations.[2] Volhard showed that the process is more under control, for analytical purposes, if a strongly basic oxide be present in the solution. Mercury, calcium, magnesium, barium and zinc salts may be used, but the latter appears to be most suitable. Meineke considered that a considerable amount of zinc sulphate 25 to 30 grms.—is needed for the

[1] A. Guyard, *Chem. News*, 8, 292, 1863; *Zeit. anal. Chem.*, 3, 373, 1864; *Bull. Soc. chim.*, (2), 1, 89, 1864; F. Jean, *ib.*, (3), 9, 248, 1893; A. Gorgeu, *ib.*, (3), 9, 490, 1893.

[2] J. Volhard, *Liebig's Ann.*, 198, 218, 1879; *Chem. News*, 40, 207, 1879; F. W. Daw, *ib.*, 79, 25, 58, 1899; T. Morawski and J. Stingl, *ib.*, 38, 297, 1878; *Journ. prakt. Chem.*, (2), 18, 96, 1878; A. Ghilian, *Rev. Univ. Mines*, (3), 3, 270, 1888; *Chem. News*, 59, 121, 1889; E. Donath, *ib.*, 43, 253, 1881; H. Brearley, *ib.*, 79, 47, 83, 1899; L. Rürup, *Chem. Ztg.*, 15, 149, 1891; A. Ledebur, *ib.*, 12, 927, 1888; 8, 829, 1884; W. Hampe, *ib.*, 7, 1104, 1883; E. Dliss, *ib.*, 34, 237, 1910; E. Donath, *ib.*, 34, 437, 1910; A. Kaysser, *ib.*, 34, 1225, 1910; R. Schöffel and E. Donath, *Oester. Zeit. Berg. Hütt.*, 31, 229, 1883; C. G. Särnström, *Berg. Hütt. Ztg.*, 40, 425, 1881; *Zeit. anal. Chem.*, 22, 84, 1883; L. Blum, *ib.*, 30, 210, 1891; M. Orthey, *ib.*, 47, 547, 1908; Z. Karaoglanoff, *ib.*, 49, 419, 1910; C. Winkler, *ib.*, 3, 423, 1864; R. Habich, *ib.*, 3, 474, 1864; W. M. Fischer, *ib.*, 48, 751, 1909; N. Wolff, *ib.*, 43, 564, 1904; *Stahl Eisen*, 4, 702, 1884; C. Reinhardt, *ib.*, 5, 782, 1885; 6, 150, 1886; C. Meineke, *Zeit. anal. Chem.*, 24, 423, 1885; *Rep. anal. Chem.*, 3, 337, 1883; 5, 1, 1885; *Zeit. angew. Chem.*, 1, 228, 1888; E. W. Mayer, *ib.*, 20, 1980, 1907; A. Longi and S. Camilla, *Gazz. Chim. Ital.*, 27, (1), 87, 1897; G. Giorgis, *ib.*, 26, (2), 528, 1896; G. C. Stone, *Journ. Amer. Chem. Soc.*, 18, 228, 1896; W. S. Thomas, *ib.*, 17, 341, 1895; W. A. Noyes, *ib.*, 24, 243, 1902; G. Auchy, *ib.*, 17, 943, 1895; 18, 498, 1896; C. T. Mixer and H. W. du Bois, *ib.*, 18, 385, 1896; E. Cahen and H. F. V. Little, *Analyst*, 36, 52, 1911; W. Heike, *Stahl Eisen*, 29, 1921, 1909; E. Müller and P. Koppe, *Zeit. anorg. Chem.*, 68, 160, 1910; P. Slawik, *Chem. Ztg.*, 36, 106, 1912; Z. Karaoglanoff, *Jahrb. Univ. Sofia*, 33, 1911; *Stahl Eisen*, 33, 633, 1913; M. Huybrechts and N. Joassart, *Bull. Soc. chim. Belg.*, 27, 130, 1913; S. Crook, *Chem. News*, 107, 157, 1913; J. G. F. Druce, *ib.*, 134, 145, 161, 1927; N. A. Valiaschko, *Journ. Russ. Phys. Chem. Soc.*, 48, 1815, 1916; P. B. Sarkar and N. R. Dhar, *Zeit. anorg. Chem.*, 121, 135, 1922; O. Hackl, *Chem. Ztg.*, 49, 257, 1925; E. de Luisi, *Met. italiana*, 17, 464, 1925; L. M. Larsen, *Chemist-Analyst*, 20, 10, 1931; E. I. Akhumov and B. B. Vasil'ev, *Zavodskaya Lab.*, 3, 407, 1934; B. Reinitzer and P. Conrath, *Zeit. anal. Chem.*, 68, 129, 1926; B. Reinitzer and F. Hoffmann, *ib.*, 77, 407, 1929; E. Wohlmann, *ib.*, 89, 321, 1932; O. B. Darbishire, *Ind. Chemist*, 3, 172, 1927; A. T. Chernuii, *Journ. App. Chem. (U.S.S.R.)*, 8, 1304, 1935. For a simple electrometric method of titration, see B. F. Brann and M. H. Clapp, *Journ. Amer. Chem. Soc.*, 51, 39, 1929.

purpose.[1] The titration can be conducted with a greater degree of precision in the presence of some zinc sulphate, and the consumption of permanganate then corresponds with:

$$3MnSO_4 + 2KMnO_4 + 2H_2O = 5MnO_2 + K_2SO_4 + 2H_2SO_4$$

Ferrous salts should be absent, since they are transformed by the permanganate into ferric salts. Bromine or hydrogen peroxide can be used to oxidise the iron, but the excess of the oxidising agent must be removed by boiling. If ferric salts be present, they can be precipitated by the addition of zinc oxide,[2] or by sodium bicarbonate, as in Särnström's method. It is somewhat difficult to see when the reaction is complete, because the manganic oxide suspended in the liquid masks the rose colour of the permanganate. The precipitate, however, coagulates on warming, and then settles quickly. Volhard's process, more or less modified, is as follows:—

Dissolution of the Material.—Dissolve a gram of the sample in a porcelain basin with a suitable acid, say, 10 c.c. of concentrated hydrochloric acid,[3] assisted, if necessary, by nitric acid,[4] particularly if sulphides be present, and ferrous iron is to be oxidised. Add 10 c.c. of concentrated sulphuric acid, and heat the mixture until the sulphuric acid fumes copiously.[5] When cold, add 25 c.c. of water and boil the solution a short time to dissolve the ferric sulphate. Transfer the mixture to a 500 c.c. flask.

Precipitation of Iron.—Nearly neutralise the solution with sodium carbonate, and, if iron be present, add gradually an emulsion of zinc oxide [6] in slight excess. Shake the mixture well after each addition, but avoid a large excess of the zinc oxide. Fill about three-fourths of the flask with water.

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[1] J. Leroide and A. Bruiltet (*Bull. Soc. chim.*, (5), **2**, 740, 1935) state that the presence of considerable alkali sulphide makes the addition of a strongly basic oxide unnecessary.

[2] The reason for this is that the p_H value of zinc hydroxide (p_H, 5·2) exceeds that of ferric hydroxide (p_H, 2·0) and also that of aluminium hydroxide (p_H, 4·14), but falls below that of manganese hydroxide (p_H, 8·8). Consequently, on adding an excess of zinc hydroxide, ferric iron and aluminium are precipitated, but not manganese—H. T. S. Britton, *Ind. Chemist*, **3**, 257, 1927.

[3] Chlorides, over 0·5 grm. per litre, should be absent, or the results will be high. If chlorides be present, the precipitate may have a reddish colour; if absent, dark brown. Evaporation with sulphuric acid until the acid fumes copiously will drive off the combined chloride.

[4] If the manganese is to be determined in the insoluble residue, fuse the insoluble matter with sodium carbonate, dissolve the resulting mass in acid and add the solution to the main solution.

[5] Organic matter should be absent. It can be destroyed by calcination, or evaporation of the solution to dryness with sulphuric acid, or with nitric acid followed by calcination.

[6] ZINC OXIDE EMULSION.—A mixture of pure zinc oxide and water will generally do the work—"generally," because some samples of commercial zinc oxide are not effective in separating iron from manganese, possibly owing to the crystalline structure of the powder. A better emulsion is made by dissolving zinc chloride in water, or by dissolving zinc oxide in hydrochloric acid, heating the mixture with a little bromine, filtering off the excess of zinc oxide and precipitating zinc hydroxide from the solution by the addition of ammonia. Do not add an excess of ammonia, or the zinc hydroxide will dissolve. Wash the precipitate several times by decantation with hot water and wash the oxide into a bottle, which is stoppered and preserved. Shake the mixture well before use. F. A. Emmerton, *Trans. Amer. Inst. Min. Eng.*, **10**, 201, 1881. A. Guyard (*Compt. rend.*, **97**, 673, 1883; *Chem. News*, **48**, 193, 1883) reports the presence of manganese in zinc oxide. L. L. de Koninck tests the suitability of the zinc oxide for the determination by triturating 3 grms. with 30 c.c. of water containing 1 grm. of iron alum in solution. The mixture is agitated with sufficient 6N-sulphuric acid to dissolve all the zinc oxide. Avoid a large excess of acid. One drop of the permanganate solution should give a permanent pink coloration. If not, metallic zinc or zinc sulphide may be present. S. Crook (*Chem. News*, **107**, 157, 1913; J. I. Hoffman, *Bur. Standards Journ. Research*, **7**, 888, 1931) recommends a double precipitation with the zinc oxide emulsion and suggests a blank to correct for errors in the water, acid and zinc oxide.

Agitate the contents of the flask [1] and let the mixture stand to allow the ferric oxide to settle. If the solution be not colourless, more zinc oxide is probably needed. Make the solution up to the mark with distilled water. Agitate the solution and let the matter in suspension settle.

The Titration.—Pipette 100 c.c. of the clear supernatant liquid into a 250 c.c. flask.[2] Heat the solution and titrate, while hot, with a standard solution of potassium permanganate. The permanganate produces a precipitate which discolours the liquid, hence it is necessary to titrate cautiously by agitating the flask after each addition and then letting the precipitate settle sufficiently to show whether or not the liquid is coloured pink.[3] The colour is best observed by holding the flask against a white background and observing whether or not the upper edges of the liquid are coloured pink. Warm (40°) the solution being titrated, but the liquid must not be boiled.[4] If the pink colour fades, add more permanganate. When the pink colour is permanent, take a final reading of the burette.

Calculation.—The permanganate is prepared by the method described on page 175. On referring to the equation on page 402, it will be seen that $2KMnO_4$ reacts with $3MnO$. Hence 1 grm. of $KMnO_4$ represents 0·6733 grm. of MnO, or 1 c.c. of N-permanganate corresponds to 0·02128 grm. of MnO.[5]

Errors.—A comparison of the results with the three processes here indicated on a commercial sample of "manganese oxide" gave:

Gibbs' phosphate process	.	74·84	74·85	74·80 per cent. MnO.
Volhard's process	.	74·68	74·66	74·56 per cent. MnO.
Pattinson's process	.	74·71	74·70	74·74 per cent. MnO.

The values by the phosphate process are probably 0·1 per cent. high. Volhard's method is inclined to give too low values when the permanganate is standardised against iron or sodium oxalate. The permanganate should be standardised against manganese sulphate of known strength.[6] Gorgeu and Carnot [7] appear to think that the low values arise from the formation of a manganous manganite—$MnO.5MnO_2$—by the manganese in the solution, and this retards the further action of the permanganate on the manganous oxide under investigation. When zinc sulphate is present, zinc manganite—$ZnO.5MnO_2$—is formed, and this leaves only part of the manganese in solution to react with the permanganate. Bemmelen [8] considers that the precipitated manganic acid adsorbs part of the manganese salts in the solution, and so removes a little manganese from the "sphere of action" of the permanganate.

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[1] Many here recommend the addition of a couple of drops of concentrated nitric acid.

[2] The precipitate in the flask may appear bulky, but, as a matter of fact, it occupies very little volume. See page 62 for a discussion on the volume of suspended precipitates. The error is here negligible.

[3] It sometimes saves time to take two aliquot portions. Titrate one by adding 1 c.c. of the permanganate at a time to obtain the approximate end-point, and in the other the titration can be carried to a greater precision without any inordinate expenditure of time. B. Reinitzer and P. Conrath (*Zeit. anal. Chem.*, 68, 129, 1926) add potassium fluoride to the solution before titration, as it assists in the flocculation and settling of the precipitate. The interference of iron, if present, is also prevented, as potassium ferrifluoride is precipitated.

[4] Owing to the well-known instability of the permanganate in the presence of the solid manganese oxide (page 179).

[5] Some workers deduct 0·2 c.c. from the volume of permanganate used in the titration before the calculation is made, in order to allow for the presence of the two drops of nitric acid which is supposed to facilitate settling and to counteract the effect of traces of organic matter.

[6] See G. Auchy, *Journ. Amer. Chem. Soc.*, 18, 498, 1896; *Chem. News*, 74, 214, 248, 262, 1896.

[7] A. Gorgeu, *Bull. Soc. chim.*, (3), 9, 490, 1893; A. Carnot, *Compt. rend.*, 116, 1375, 1893.

[8] J. M. van Bemmelen, *Journ. prakt. Chem.*, (2), 23, 387, 1888.

He further assumes that when a zinc salt is present the zinc salt is adsorbed instead of the manganese salt.

The chief errors arise from the presence of organic matter; the addition of too much zinc oxide; and standardising the permanganate against iron instead of against manganese reduced from permanganate. Cobalt and chromium interfere with the process.[1]

The method gives good results with compounds rich in manganese, although some object to the process, saying it gives erratic results. This criticism is too severe; when the peculiarities of the method are understood, it is reliable, and some analysts have said that they consider it to be "the simplest, quickest and most accurate process for the volumetric determination of manganese."

Fischer's Modification of Volhard's Process. - This process, as recommended by Cahen and Little,[2] is as follows:- The solution of the manganese salt in hydrochloric or sulphuric acid is neutralised with caustic soda until a slight precipitate persists on shaking. The precipitate is just redissolved by the addition of a drop or two of dilute sulphuric acid. Add 10 grms. of zinc sulphate and heat the mixture to boiling. Add 1 grm. of freshly ignited zinc oxide, and titrate with permanganate, frequently heating nearly to boiling, until the permanganate is no longer decolorised. Cool the mixture under the tap for a minute or two, add 1-2 c.c. of glacial acetic acid and thoroughly agitate the solution. The hot (not boiling) liquid is then titrated with permanganate, added a few drops at a time, with vigorous shaking after each addition, until the supernatant liquid retains its pink colour after being well shaken several times. The end-point is easily observed, because the precipitate settles very quickly in the presence of acetic acid.

A difficulty arises during the titration unless the volume of the permanganate is known to within 3 or 4 c.c., owing to the slowness with which the finely divided oxide settles in the presence of zinc oxide. The time required for a titration is very long, and the end-point is difficult to detect. If the acetic acid be added before any permanganate is added the result is too low, but the titration is rapidly effected and the result serves as a guide for the titration proper.

The results leave little to be desired as far as accuracy is concerned. With two samples of pyrolusite, the following comparative results were obtained:

	No. 1.	No. 2.
Volhard-Fischer's process	48·75	50·35
Pattinson's process	48·72	50·50

§ 196. The Evaluation of Manganese Dioxide—Mohr's Process.

Manganese ores were formerly evaluated on the amount of oxygen in excess of that in the monoxide, since the dioxide ores were alone considered worth working. The content of manganese is sought by principal buyers and the lower oxides are now considered of more value than the others. The source of pottery manganese colours is a pyrolusite ore, although the lower oxides would do quite as well or better if equally free from other colouring oxides—say iron oxide.

By the simultaneous action of sulphuric acid and an excess of ferrous sulphate or oxalic acid, the manganese dioxide is reduced to manganous sulphate

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[1] For a list of salts in the presence of which the determination can be accurately carried out, see P. B. Sarkar and N. R. Dhar—*Zeit. anorg. Chem.*, **121**, 135, 1922.

[2] E. Cahen and H. F. V. Little, *Analyst*, **36**, 52, 1911.

and the ferrous sulphate or oxalic acid is simultaneously oxidised. Known quantities of ferrous sulphate or oxalic acid are used, and the excess, not oxidised, can be determined by titration with standard permanganate.[1] The reaction with oxalic acid is represented:

$$MnO_2 + H_2C_2O_4 + H_2SO_4 = MnSO_4 + 2CO_2 + 2H_2O$$

The following operations furnish sufficient data to calculate the amount of the manganese dioxide in the given sample.

The Determination.—Digest 1·0 grm. of finely divided, dry (110°)[2] sample in an Erlenmeyer's flask with 30 c.c. of a 1·0N-oxalic acid[3] or sodium oxalate solution, and 100 c.c. of sulphuric acid (1 : 4), until the black particles have passed into solution. Add about 100 c.c. of hot water (70°), and titrate the warm solution with approximately 1·0N-potassium permanganate until a permanent pink blush is suffused throughout the liquid. If, and when, a brown precipitate appears during the titration, the latter must be stopped and the solution shaken until the precipitate clears off. Since permanganate solutions are apt to lose strength on standing, the oxalic acid equivalent of the permanganate solution must be ascertained by making a blank titration on 30 c.c. of the 1·0N-oxalic acid solution, in the presence of dilute sulphuric acid and hot water, as indicated above.[4]

Calculation.—From the above equation it follows that 90·016 grms. of anhydrous oxalic acid, or 2000 c.c. of 1·0N-oxalic acid solution, are oxidised by 86·93 grms. of MnO_2. Alternatively, 0·043465 grm. of MnO_2 will oxidise 1 c.c. of 1·0N-oxalic acid.

Suppose, in an experiment, that in the blank titration 30·0 c.c. of 1·0N-oxalic acid are oxidised by 30·5 c.c. of the permanganate solution and that in the main titration 12·2 c.c. of permanganate are needed to oxidise the excess of 1·0N-oxalic acid.

Then, since 30·5 c.c. of permanganate oxidise 30·0 c.c. of 1·0N-oxalic acid, 12·2 c.c. of permanganate will oxidise 30·0 × 12·2/30·5 = 12·0 c.c. of 1·0N-oxalic acid. Hence (30·0 12·0) = 18·0 c.c. of 1·0N-oxalic acid have been oxidised by the one gram sample of manganese dioxide. Consequently 100 grms. of the sample will oxidise 1800 c.c. of 1·0N-oxalic acid, which is equivalent to 1800 × 0·043465 = 78·2 per cent. of MnO_2.

Errors.—The process indicated above represents the amount of oxygen— "available oxygen"—which is given off when the sample is decomposed by

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[1] W. Hempel, *Mémoire sur l'emploi de l'acide oxalique dans les dosages à liqueurs titrées,* Lausanne, 1853; F. Mohr, *Zeit. anal. Chem.,* 8, 314, 1869. R. Fresenius and H. Will (*Neue Verfahrungsweise zur Prüfung der Potasche, etc., sowie des Braunstein,* Heidelberg, 1843) determined the amount of manganese dioxide from the loss in weight due to the evolution of carbon dioxide; H. Kolbe (*Liebig's Ann.,* 119, 130, 1861) absorbed the carbon dioxide in weighed potash bulbs; G. Bodländer (*Zeit. angew. Chem.,* 7, 430, 1894) measured the volume of the gas evolved during the action of acid. O. L. Barnebey (*Journ. Ind. Eng. Chem.,* 9, 961, 1917) says that oxalic acid is decomposed while heating the ore to decompose it. E. Rupp (*Arch. Pharm.,* 254, 135, 1916; *Chem. Ztg.,* 52, 429, 1928; O. L. Barnebey and W. C. Hawes, *Journ. Amer. Chem. Soc.,* 39, 607, 1917; O. L. Barnebey and G. M. Bishop, *ib.,* 39, 1235, 1917) treats the finely powdered sample with acid and alkali iodide and titrates the liberated iodine with thiosulphate.

[2] The sampling in bulk for moisture requires special attention (page 110). J. E. de Vry, *Liebig's Ann.,* 61, 248, 1847; R. Fresenius, *Dingler's Journ.,* 135, 277, 1855.

[3] Or 1·9 to 2·0 grms. of the hydrated acid—$H_2C_2O_4.2H_2O$. A normal solution of oxalic acid contains 63·024 grms. of the hydrated acid per litre, equivalent to 45·008 grms. of the anhydrous acid. For the preparation of the pure hydrated acid, see W. D. Treadwell and H. Johner, *Helv. Chim. Acta,* 7, 528, 1924.

[4] For the accuracy of permanganate-oxalic acid titrations, see I. M. Kolthoff, *Pharm. Weekblad,* 61, 417, 1924; *Zeit. anal. Chem.,* 64, 185, 1924.

oxalic acid, and since other manganese oxides—*e.g.* Mn_2O_3, Mn_3O_4—react in a similar way with oxalic and sulphuric acids—

$$Mn_2O_3 + 2H_2SO_4 + H_2C_2O_4 = 2MnSO_4 + 3H_2O + 2CO_2$$
$$Mn_3O_4 + 3H_2SO_4 + H_2C_2O_4 = 3MnSO_4 + 4H_2O + 2CO_2$$

it follows that, if these oxides be present, the calculation might indicate more MnO_2 and less MnO than is really present. Some of the calculated MnO_2 might be present as Mn_2O_3 or Mn_3O_4. If the total manganese, calculated as MnO, be determined as described on page 399 or 401—Pattinson's or Volhard's process—and the amount of MnO_2, multiplied by 0·816, be subtracted from it, then the difference will represent the approximate amount of manganous oxide —MnO—in the sample. If the pyrolusite contains reducing agents—*e.g.* ferrous oxide or carbonaceous matter— low results will be obtained, because reactions are set up which reverse that produced by the peroxide.

Any ferrous iron which might be present will react with the permanganate and give low results by apparently diminishing the amount of oxalic acid oxidised by the manganese dioxide.[1] Carbonates do not interfere.

§ 197. The Colorimetric Determination of Manganese — Walter's Process.

The colorimetric determination of manganese is based upon the ease with which manganese solutions are oxidised to pink or violet permanganate. Brunner[2] fused the sample with alkali, while exposed to an oxidising atmosphere, and deduced the amount of manganese from the intensity of the colour of the solution of the fused cake. The results by this method are not satisfactory, and oxidising agents are used to convert the manganese into the purplered permanganate. Lead peroxide[3] was proposed for this purpose by Crum in 1845, Schneider proposed sodium bismuthate[4] in 1888, H. Marshall

[1] *Cf.* H. Ditz, *Zeit. anorg. allgem. Chem.*, **219**, 113, 1934.

[2] A. Brunner, *Dingler's Journ.*, **210**, 278, 1873.

[3] W. Crum, *Liebig's Ann.*, **55**, 219, 1845; W. Gibbs, *Amer. J. Science*, (2), **14**, 205, 1852; T. M. Chatard, *ib.*, (3), **1**, 419, 1871; *Chem. News*, **24**, 196, 1871; S. Peters, *ib.*, **33**, 35, 1876; *Dingler's Journ.*, **221**, 486, 1876; P. Picard, *Compt. rend.*, **75**, 1821, 1872; A. Leclerc, *ib.*, **75**, 1209, 1872; *Chem. News*, **26**, 296, 1872; L. L. de Koninck, *Rev. Univ. Mines*, (3), **5**, 308, 1889; T. E. Thorpe and F. J. Hambly, *Journ. Chem. Soc.*, **53**, 182, 1888; A. Ledebur, *Berg. Hütt. Ztg.*, **41**, 417, 1882; F. C. G. Müller, *Stahl Eisen*, **6**, 98, 1886; F. Osmond, *Bull. Soc. chim.*, (2), **43**, 56, 1885; V. Deshays, *Chem. News*, **38**, 70, 1878; C. D. Braun, *Zeit. anal. Chem.*, **7**, 342, 1868; J. Volhard, *Liebig's Ann.*, **198**, 357, 1879; F. Hoppe-Seyler, *Journ. prakt. Chem.*, (1), **90**, 303, 1863; H. W. Vogel, *Ber.*, **8**, 1534, 1875; R. Fresenius, *Zeit. anal. Chem.*, **11**, 303, 1872; L. Dobbin, *Journ. Soc. Chem. Ind.*, **35**, 80, 1916; L. Schneider, *Chem. Ztg.*, **21**, 41, 1897; E. I. Dyrmont, *Journ. Russ. Phys. Chem. Soc.*, **48**, 1807, 1916; R. Wasmuht, *Zeit. angew. Chem.*, **42**, 133, 1929; L. A. Congdon and J. L. Neal, junr., *Chem. News*, **128**, 67, 1924.

[4] L. Schneider, *Monats.*, **9**, 252, 1888; *Dingler's Journ.*, **269**, 224, 1893; L. Dufty, *Chem. News*, **84**, 248, 1901; J. Reddrop and H. Ramage, *Journ. Chem. Soc.*, **67**, 268, 1895; F. Ibbotson and H. Brearley, *Chem. News*, **82**, 269, 1900; **84**, 247, 302, 1901; **85**, 58, 1902; H. Ramage, *ib.*, **84**, 209, 269, 1901; **85**, 24, 95, 1902; A. A. Blair, *Journ. Amer. Chem. Soc.*, **26**, 793, 1904; R. S. Weston, *ib.*, **29**, 1074, 1907; F. J. Metzger and R. F. M'Cracken, *ib.*, **32**, 1250, 1910; R. S. McBride, *ib.*, **34**, 415, 1912; W. Blum, *ib.*, **34**, 1379, 1912; P. H. M. P. Brinton, *Journ. Ind. Eng. Chem.*, **3**, 237, 376, 1911; W. F. Hillebrand and W. Blum, *ib.*, **3**, 374, 1911; D. J. Demorest, *ib.*, **4**, 19, 1912; J. R. Cain, *ib.*, **3**, 360, 1911; G. Bertrand, *Bull. Soc. chim.*, (4), **9**, 361, 1911; H. Rubricus, *Stahl Eisen*, **30**, 957, 1910; R. A. Gortner and C. O. Rost, *Journ. Ind. Eng. Chem.*, **4**, 522, 1912; F. J. Metzger and L. E. Marrs, *ib.*, **3**, 333, 1911; **5**, 125, 1913; H. F. V. Little, *Analyst*, **37**, 554, 1912; C. T. Nesbitt, *Chem. News*, **115**, 61, 1917; H. Kinder, *Stahl Eisen*, **37**, 197, 1917; G. E. F. Lundell, *Journ. Amer. Chem. Soc.*, **45**, 2600, 1923; T. R. Cunningham and R. W. Coltman, *Ind. Eng. Chem.*, **16**, 58, 1924; B. Park, *ib.*, **18**, 597, 1926; T. Somiya, *Journ. Soc. Chem. Ind. Japan*, **33**, 255B, 1930; L. A. Congdon and J. L. Neal, junr., *Chem. News*, **128**, 67, 1924; D. Lombardo, *Met. Ital.*, **26**, 705, 1934; J. I. Hoffman, *Bur. Standards Journ. Research*, **7**, 888, 1931.

ammonium persulphate [1] in 1901, Willard and Greathouse recommended alkali periodates in 1917,[2] and nickel dioxide [3] was used by Lang in 1926. The manganese in the given solution is thus oxidised to pink permanganic acid. The intensity of the coloration depends upon the amount of manganese present. The tint of a test solution so prepared can be compared with the tint of a similar solution containing a known amount of manganese. Something of the order of 0·00001 grm. of manganese in 100 c.c. of solution can be determined by this process.

Preparation of the Standard Solution.—A stock solution of manganese sulphate containing 0·1 grm. of MnO per litre is prepared. Dissolve 0·3145 grm. of pure manganous sulphate—$MnSO_4.4H_2O$—in water, acidify with a few c.c. of concentrated sulphuric acid and make the solution up to a litre. Pipette sufficient of this solution—say 5 c.c.—into a 100 c.c. flask. Add 10 c.c. of a 0·2 per cent. solution of silver nitrate, add 1 grm. of ammonium persulphate and warm on a water bath until a pink colour is developed. By the time the flask has cooled the colour will have acquired its maximum intensity. Make up to the 100 c.c. mark. Pipette from 2 to 10 c.c. into the test glass of the colorimeter.

If insufficient silver nitrate has been added, a brown precipitate of manganese peroxide will be produced in the solution after the addition of the ammonium persulphate. In that case, add sulphurous acid until the precipitate is dissolved and then add more silver nitrate. Reoxidise with ammonium persulphate as before.[4]

The Test Solution.—The solution obtained by dissolving the cake from the pyrosulphate fusion, or the solution remaining after the colorimetric titanium determination, may be used; or the manganese sulphide can be dissolved in dilute sulphuric acid. The products from the pyrosulphate fusion generally

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[1] H. E. Walters, *Proc. Eng. Soc. West Pa.*, **17**, 257, 1901; *Journ. Amer. Chem. Soc.*, **25**, 392, 1903; **27**, 1550, 1905; *Chem. News*, **84**, 239, 1901; H. Marshall, *ib.*, **83**, 73, 1901; *Journ. Soc. Chem. Ind.*, **16**, 399, 1897; M. R. Schmidt, *Journ. Amer. Chem. Soc.*, **32**, 965, 1910; J. V. R. Stehman, *ib.*, **24**, 1204, 1902; H. Rubricus, *Stahl Eisen*, **30**, 957, 1910; H. Kunze, *ib.*, **32**, 1914, 1912; P. Holland, *Chem. News*, **96**, 2, 1907; J. J. Boyle, *Journ. Ind. Eng. Chem.*, **4**, 202, 1912; M. Stanichitch, *Rev. Met.*, **8**, 891, 1911; E. Schowalter, *Zeit. Nahr. Genuss*, **26**, 104, 1913; **27**, 553, 1914; F. Haas, *ib.*, **25**, 392, 1913; L. Hartwig and H. Schellbach, *ib.*, **26**, 439, 1913; C. W. Wright, *Chem. News*, **108**, 248, 1913; H. Lührig, *Chem. Ztg.*, **38**, 781, 1914; W. W. Clark, *Met. Chem. Eng.*, **13**, 155, 1915; C. H. Fleckinger, *Chemist-Analyst*, **14**, 7, 1915; L. Dobbin, *Journ. Soc. Chem. Ind.*, **35**, 80, 1916; J. Williams, *Chem. News*, **99**, 288, 1909; A. Travers, *Compt. rend.*, **165**, 187, 1917; *ib.*, **182**, 972, 1088, 1926; *Ann. Chim.*, (10), **6**, 56, 1926; D. H. Wester, *Rec. Trav. chim.*, **39**, 414, 600, 1920; J. Vernay, *Chim. et Ind.*, **11**, 1093, 1924; L. A. Congdon and J. L. Neal, junr., *Chem. News*, **128**, 67, 1924; K. Swoboda, *Zeit. anal. Chem.*, **64**, 156, 1924; O. Hackl, *ib.*, **105**, 81, 1936; C. Newcomb, *Analyst*, **53**, 644, 1928; T. Somiya, *Journ. Soc. Chem. Ind. Japan*, **33**, 255B, 1930; *Chem. News*, **141**, 129, 1930; J. H. van der Meulen, *Chem. Weekblad*, **28**, 377, 1931; J. H. D. Bradshaw, *Foundry Trade Journ.*, **44**, 311, 1931; R. Lang and F. Kurtz, *Zeit. anal. Chem.*, **85**, 181, 1931; A. C. Janzig, *Journ. Amer. Waterworks Assocn.*, **18**, 744, 1927; F. Alten and H. Weiland, *Zeit. Pflanz. Düngung Bodenk.*, **30A**, 193, 1933; S. N. Rozanov and D. V. Voskresenskaya, *ib.*, **35A**, 140, 1934; M. Korenman, *Mikrochemie*, **15**, 289, 1934.

[2] H. H. Willard and L. H. Greathouse, *Journ. Amer. Chem. Soc.*, **39**, 2366, 1917; T. G. Thompson and T. L. Wilson, *ib.*, **57**, 233, 1935; H. H. Willard and J. J. Thompson, *Ind. Eng. Chem. Anal. Ed.*, **3**, 399, 1931; G. J. Hough, *ib.*, **7**, 408, 1935.

[3] R. Lang, *Zeit. anorg. Chem.*, **158**, 370, 1926.

[4] A. Travers (*Ann. Chim.*, (10), **6**, 56, 1926) says that when the amount of manganese exceeds 2·5 grms. per litre, metaphosphoric acid should be added to the solution before oxidation to prevent the formation of the brown peroxide. According to A. I. Appelbaum (*Chemist-Analyst*, **17**, 22, 1916; A. Travers, *l.c.*; A. Pinkus and L. Ramakers, *Bull. Soc. chim. Belg.*, **41**, 529, 1933) the silver oxide, Ag_2O, is oxidised to silver peroxide, Ag_2O_2, by the ammonium persulphate.

contain traces of chlorides, which must be removed before applying the test.[1] Hence it is usually quickest to assume that chlorides are present. Pipette out, say, 50 c.c. of the stock solution, resulting from the pyrosulphate fusion, boil and add a little silver nitrate solution. Filter and wash the precipitate. Collect the filtrate and washings in a 100 c.c. flask; acidify the solution with sulphuric acid; add 10 c.c. of the silver nitrate solution, 1 grm. of ammonium persulphate and warm as indicated above for the preparation of the standard solution. When the solution is cold, make it up to the mark with water and pour a portion of it into the test glass of the colorimeter.

The Comparison.— An aliquot portion of the standard permanganate solution is diluted with water from a burette until it has the same tint as the test solution. The amount of water required for the purpose is measured. See titanium, page 189, for further details.

Calculation.— Suppose that 5 c.c. of the standard solution of manganese sulphate was oxidised and then diluted to give 100 c.c. of the standard permanganate solution, and that 10 c.c. of the latter solution required the addition of 21 c.c. of water to bring to the same tint as the test solution.

1 c.c. standard has 0·0001 grm. MnO; $\therefore$ 5 c.c. have 0·0005 grm.; this diluted to 100 c.c. has 0·000005 grm. MnO per c.c. : 10 c.c. of this required 21 c.c. water, so that $10 + 21 = 31$ c.c. of the solution has 0·00005 grm. MnO.

Hence every 31 c.c. of the test solution contains 0·00005 grm. MnO. Thus 100 c.c. of the test solution contains $100 \times 0·00005/31$ grm. MnO. Now the test solution was made up from 50 c.c. of the stock solution, consequently the 250 c.c. of stock solution contains $100 \times 0·00005 \times 5/31$ grm. MnO. But the stock solution was obtained from 1 grm. of the clay, and therefore the clay contains $100 \times 0·00005 \times 5 \times 100/31 = 0·08$ per cent. MnO. In general, with the dilutions given above, the percentage of MnO in a clay is given by $2·5/(10 + v)$, where v is the number of c.c. of water used to dilute 10 c.c. of the standard permanganate solution to the same tint as the test solution.

With practice, and normal colour vision, differences of tint corresponding with 0·00001 grm. of MnO can be detected.[2] If the quantity of manganese in the portion of the sample under investigation is less than 0·001 grm., it is well to work with a larger quantity of the sample. The results with quantities of manganese over about 2 per cent. are not so good as by gravimetric or volumetric processes. The presence of a little iron seems to favour the oxidation of the manganous oxide, MnO, to the permanganate.[3] Aluminium and molybdenum do not interfere; copper and nickel exercise no further influence than that due to the colour of their salts.

The Effect of Chromium Salts.— If chromium be present, the yellow colour of the chromate produced by the oxidising action of the persulphate alters the tint of the permanganate, and the chromium must be removed before the comparison can be made. Dittrich[4] does this by boiling the oxidised solution with ammonia for a short time—iron and manganese hydroxides are precipitated, and the chromium remains in solution as chromate. Filter and wash. The precipitate on the filter-paper is dissolved in dilute sulphuric acid, mixed with

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[1] According to G. Denigès (*Compt. rend.*, **194**, 91, 1932), it is unnecessary to remove chlorides if the solution is oxidised with hypochlorite or hypobromite in the presence of copper sulphate as catalyst. In this way 1 to 2 mgrms. of manganese per litre of 10 per cent. chloride solution can be detected.

[2] See H. Forestier (*Bull. Soc. chim.*, (4), **33**, 659, 1923) for the use of nickel sulphate solution as a light filter in the colorimetric comparison.

[3] Compare H. Jervis, *Chem. News*, **81**, 171, 1900.

[4] M. Dittrich, *Zeit. anorg. Chem.*, **80**, 171, 1913. See F. C. T. Daniels (*Journ. Ind. Eng. Chem.*, **6**, 658, 1914) for an alternative method.

some sulphurous acid or hydrogen peroxide. The manganese is then determined colorimetrically as indicated above. Remove the silver from the filtrate by the addition of common salt; again filter and wash. Evaporate the filtrate down to between 50 and 100 c.c. and determine the chromium as indicated on page 526.

The Effect of Titanium.—Hough states that if more than about 1 per cent. of titanium dioxide is present in solution, ammonium persulphate is useless as the oxidising agent since no colour is developed unless excessive amounts of the reagents are present and even then there is no guarantee that the maximum coloration is obtained.[1] In such cases the use of sodium bismuthate or preferably potassium periodate as the oxidising agent is recommended.

§ 198. The Analysis of Wads and Manganese Earths.

Manganese peroxide is mainly used in the manufacture of chemicals, in glass-making and for the manufacture of dry batteries. There are many manganese ores which serve excellently for the manufacture of pottery colours and yet contain little or no peroxide. Mohr's process is not then applicable. These ores are usually sold on a basis of 50 units of manganese [2]—one unit means 1 per cent.—at so much per unit, with a bonus or penalty per unit respectively above or below 50. A maximum of, say, 8 per cent. silica and 0·2 per cent. phosphorus may be allowed, with an agreed deduction for each unit of silica and for each 0·02 per cent. of phosphorus above these respective maxima.[3] The Caucasian, Indian and Brazilian ores are fairly constant in composition and run from about 50 to 55 per cent. manganese, 0·03 per cent. phosphorus and 10 per cent silica; the Turkish and Japanese ores run from 43 to 56 per cent. manganese, 0·5 per cent. phosphorus and 7 to 10 per cent. silica. Japanese "brown stone" may run as much as 87 per cent. MnO_2, and such an ore sells for twice as much as 70 per cent. ore.[4]

Dissolution of the Sample.—Digest 1 grm. of the sample in a 250 c.c. Erlenmeyer's flask with 10 c.c. concentrated hydrochloric acid. The attack generally begins in the cold. When the first action is over, gradually warm the flask up to the boiling-point. It may be necessary to add a little more acid to complete the action. Add water and filter. The insoluble matter may be light-coloured silica or some dark-coloured mineral not decomposed by the acid. The filter-paper and contents should be ignited in a weighed platinum crucible and weighed. This may be reported as "sand and insoluble matter," or fused with alkali carbonate in an oxidising atmosphere. If the mass on cooling is white or only pale greenish-blue in tinge, it may be rejected. If the fused mass be green, dissolve in hydrochloric acid, evaporate to dryness and take up with water and hydrochloric acid as indicated on page 144. Add the filtrate from the silica to the main solution. The silica may be determined in the usual manner.

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[1] G. J. Hough, *Ind. Eng. Chem. Anal. Ed.*, **7**, 408, 1935. Compare O. Hackl, *Zeit. anal. Chem.*, **105**, 182, 1936.

[2] Pure manganous oxide, MnO, runs 77·5 per cent. manganese (Mn); the dioxide, MnO_2, 63·2 per cent.; the sesquioxide, Mn_2O_3, 69·6 per cent.; and the manganomanganic oxide, Mn_3O_4, 72·0 per cent.

[3] *E.g.* one consumer purchased his ore on the following basis (1911): Ores with 50 per cent. Mn to be purchased (delivered) at 13d. per unit per ton; 46–50 per cent. Mn, 12¼d.; 43–46 per cent. Mn, 12d; 40–43 per cent., 11¼d. For each per cent. of silica above a maximum of 8 per cent., deduct 7¼d. per ton, and for each 0·02 per cent. phosphorus above 0·2 per cent., deduct 1d. per unit of manganese per ton. Sample for analysis to be dried at 100°; the percentage of moisture in the sample to be deducted from the weight.

[4] G. T. Holloway, *Trans. Inst. Min. Met.*, **21**, 569, 1912.

Removal of Alumina and Iron Oxide.—Precipitate the joint alumina, ferric oxide and phosphoric oxide by the sodium acetate process (page 383) from a solution acidified with acetic acid. If much manganese be present, two, three or four precipitations may be necessary. If the combined filtrates exceed 300 c.c., evaporate to about 200 c.c. If a white precipitate separates during the evaporation, it may be neglected; but if a reddish precipitate separates, it must be filtered off, dissolved in hydrochloric acid, the iron precipitated as basic acetate and the filtrate added to the main filtrate. The alumina, iron and phosphoric oxide may be treated by the methods of page 157

Precipitation of Manganese.—Add approximately 5 grms. of sodium acetate —15 c.c. of solution [1]—and 2 or 3 c.c. of liquid bromine. If a saturated aqueous solution of bromine be used, the solution may become rather bulky. The solution should have a yellow tint, showing that an excess of bromine is present. Boil, then filter. Add more bromine to the filtrate and boil again. This ensures the complete precipitation of the manganese. If any precipitate be formed, filter. The precipitated manganese is dissolved in hot dilute nitric acid to which is added either sulphurous acid or a little sodium bisulphite. The reducing agent facilitates the solution of the precipitate. The manganese may now be determined in the solution by volumetric, colorimetric or gravimetric processes. If needed, the lime and magnesia can be determined in the combined filtrates.

Determination of Carbon.—Dissolve 10 to 20 grms. of the ore in concentrated hydrochloric acid as indicated above. Dilute with water. Filter the residue through a Gooch crucible charged with ignited asbestos, wash, dry at 110° and weigh the crucible and contents. Burn off the carbon and re-weigh. The loss in weight represents the organic matter. To eliminate the obvious errors, the asbestos may be ignited and the resulting carbon dioxide determined as indicated on page 631. The wet combustion process may also be used as indicated on page 616.

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[1] See footnote 7, page 383.

CHAPTER XXIX.

THE DETERMINATION OF COBALT AND NICKEL.

§ 199. The Detection of Cobalt and Nickel.

THE usual scheme for the qualitative analysis of mixtures leaves finally a precipitate containing the mixed sulphides of cobalt and nickel. There are several distinguishing tests. To get the sulphides into solution, boil the filter paper and contents in a small flask with 10 c.c. of hydrochloric acid (1 : 4) and 1 c.c. of nitric acid (1 : 3). Filter off the precipitated sulphur and the filter-paper. Collect the filtrate in a basin and evaporate to dryness to expel the excess of acid. Dissolve the residue in two or three drops of hydrochloric acid and 10 c.c. of water.

Tests for Cobalt. (1) *Ilinsky and Knorre's Test.*[1]—Add a slight excess of a saturated solution of α-nitroso-β-naphthol (page 420) in acetic acid. Agitate the solution. A brick-red precipitate indicates cobalt. Confirm as usual. Atack uses the sodium salt of α-nitroso-β-naphthol in the presence of dilute sulphuric acid and claims that 0·001 mgrm. of cobalt can be detected per c.c. by the orange-red colour produced. The test can be used in the presence of nickel, ferric, manganese and zinc salts and also of citric and tartaric acids. If very large quantities of nickel are present, it should be removed.

(2) *Skey's Test.*[2]—Add a saturated solution of potassium thiocyanate and shake up the mixture with a mixture of amyl alcohol and ether. The ethereal layer will be blue if 1 c.c. of a 1 : 50,000 aqueous solution be used.

(3) *Danziger's Test.*[3]—To about 5 c.c. of the colourless solution, acidified with hydrochloric acid, add a little solid ammonium thioacetate—CH_3. $COSNH_4$—a few drops of stannous chloride,[4] and an equal volume of amyl alcohol, or a mixture of acetone and ether, or alcohol and ether. Shake. Let settle. If cobalt be present, the upper layer will be coloured blue. This test will indicate 1 part of cobalt in 500,000 parts of water, and is more delicate than Skey's test.

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[1] M. Ilinsky and G. von Knorre, *Ber.*, **18**, 699, 1885; F. W. Atack, *Journ. Soc. Chem. Ind.*, **34**, 641, 1915; F. Feigl and R. Stern, *Zeit. anal. Chem.*, **60**, 1, 1921; I. Bellucci (*Gazz. Chim. Ital.*, **49**, (2), 294, 1919) claims that β-nitroso-α-naphthol is a vastly more sensitive reagent than α-nitroso-β-naphthol.

[2] W. Skey, *Chem. News*, **16**, 201, 1867. This is generally, but incorrectly, called "Vogel's test." H. W. Vogel, *Ber.*, **8**, 1533, 1875; **12**, 2314, 1879; F. P. Treadwell, *Zeit. anorg. Chem.*, **26**, 108, 1901; H. Ditz, *Chem. Ztg.*, **46**, 121, 1922; F. J. Allen and A. R. Middleton, *Proc. Indiana Acad. Sci.*, 147, 1922; I. F. P. Dwyer, *Austral. Chem. Inst. Journ. and Proc.*, **3**, 239, 1936. See page 427.

[3] J. L. Danziger, *Journ. Amer. Chem. Soc.*, **24**, 578, 1902; *Zeit. anorg. Chem.*, **32**, 78, 1902.

[4] To reduce the ferric salts which give a red colour. The solid ammonium thioacetate ensures a concentrated solution.

(4) *Uhlenhuth's Test.*— Uhlenhuth [1] found sodium 1 : 2-diaminoanthra-quinone-3-sulphonate gave a blue coloration with copper when other tests gave no indication of the metal. Malatesta and di Nola find that cobalt and nickel also give colorations. They use a solution containing 0·5 grm. of the reagent, 100 c.c. of concentrated aqua ammonia, 360 c.c. of water and 40 c.c. of 40 per cent. sodium hydroxide. All three metals give a blue coloration. On adding concentrated aqua ammonia, the nickel blue turns reddish-violet; with ammonium chloride, the copper blue becomes red; the cobalt blue is not changed by either reagent. It is claimed that 2×10^{-7} grm. of cobalt and 5×10^{-6} grm. of nickel can be so detected.

(5) *Van Klooster's Test.* [2]—Add 1 grm. of sodium acetate and 2 c.c. of a 0·5 per cent. aqueous solution of nitroso-R salt- $C_{10}H_4.OH.NO.(NaSO_3)_2$ - to 2 c.c. of the faintly acid test solution. Heat to boiling, add gradually 1 c.c. of concentrated nitric acid and boil for one minute. A permanent red colour indicates cobalt; the colours produced by other metals, *e.g.* iron and nickel, are destroyed by the nitric acid.

(6) *Chiarottino's Test.* [3]—To the neutral solution add a few c.c. of a solution containing 0·5 grm. of benzidine and 0·25 grm. of dimethylglyoxime in 100 c.c. of 95 per cent. alcohol. The development of an orange-red colour shows the presence of cobalt. The test is said to detect 0·01 mgrm. of cobalt. If nickel be present it must first be removed by adding excess of dimethylglyoxime and filtering off the precipitate. Copper and chromium interfere with the test.

Tests for Nickel. (1) *Tschugajeff's Test.* [4]—If an excess of dimethylgly-oxime be added to a strongly ammoniacal solution containing a mixture of cobalt and nickel, and the solution be boiled a short time, a rose coloration or a scarlet-red precipitate will be obtained, according to the amount of nickel present (page 421). This reagent is reported to detect nickel in 1 c.c. of a 1 : 200,000 solution, or in 4 c.c. of a 1 : 500,000 solution.

(2) *Atack's Test.* [5]—The solution, which should not contain more than about 0·025 grm. of metal, is made slightly ammoniacal. If nickel is present, a red precipitate is formed on treating the solution with an alcoholic solution of α-benzil dioxime. The result is not affected by cobalt. Nitrates interfere and should be removed by evaporation with sulphuric acid.

(3) *Pozzi-Escot's Test.* [6]—Nickel molybdate, formed by the action of an alkali molybdate on a nickel salt, is insoluble in neutral or feebly acid solutions which contain an excess of the precipitant, while cobalt molybdate is soluble under the same conditions. The solution of the mixed sulphides in aqua regia is nearly neutralised with alkali, treated with a large excess of a saturated solution of ammonium molybdate and heated with shaking at 70°. An opalescence is given by as little as 0·01 grm. of nickel in the presence of

[1] R. Uhlenhuth, *Chem. Ztg.*, **34**, 887, 1910; G. Malatesta and E. di Nola, *Boll. Chim. farm.*, **52**, 819, 855, 1913.

[2] H. S. van Klooster, *Journ. Amer. Chem. Soc.*, **43**, 746, 1921.

[3] A. Chiarottino, *Industria chimica*, 8, 32, 1933; A. W. Scott, *Journ. Amer. Chem. Soc.*, **55**, 3647, 1933.

[4] L. Tschugajeff, *Ber.*, **38**, 2520, 1905. For the sensitiveness of different tests for cobalt and nickel, see A. del Campo y Cerdan and J. Ferrer, *Anales Soc. Espan. Fis. Quim.*, **9**, 201, 272, 1911; S. R. Benedict, *Journ. Amer. Chem. Soc.*, **27**, 1360, 1905; R. H. Kerr, *Journ. Ind. Eng. Chem.*, **6**, 207, 1914; A. R. Middleton and H. L. Miller, *Journ. Amer. Chem. Soc.*, **38**, 1705, 1916; F. Feigl, *Ber.*, **57B**, 758, 1924; F. Feigl and L. von Tustanowska, *ib.*, **57B**, 762, 1924; C. G. Vernon, *Chem. News*, **126**, 200, 1923; C. C. Palit, *ib.*, **128**, 293, 1924; S. J. Tindal, *ib.*, **130**, 34, 1925. See also footnote 1, page 422.
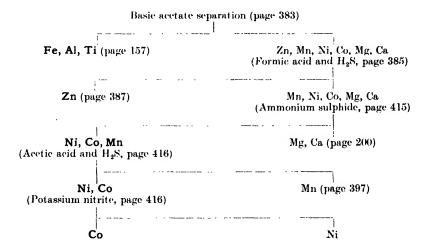
[5] F. W. Atack, *Analyst*, **38**, 316, 1913; *Chem. Ztg.*, **37**, 773, 1913; *Journ. Chem. Soc.*, **108**, 1317, 1913.

[6] M. E. Pozzi-Escot, *Compt. rend.*, **145**, 435, 1907.

500 times its weight of cobalt.　Cobaltammine salts give a precipitate, and hence such ammines must first be converted into cobalt salts.

(4) *Parr's Test*.[1] - Freshly precipitated nickel hydroxide liberates iodine from potassium iodide, but the corresponding cobalt compound does not. Hence add bromine water to the solution containing either cobalt or nickel; warm the solution; add an excess of sodium hydroxide, and boil.　Filter. Wash the precipitated hydroxide on the filter-paper.　Pour a hot solution of potassium iodide through the paper.　Free iodine in the filtrate is evidence of nickel.　The iodine is best detected by shaking up the filtrate with a little benzene.

The separation of cobalt and nickel is not usually of any particular importance in silicate analyses, but the methods here indicated represent the type of thing wanted in colour and glaze analyses.　The analysis of cobalt oxides is more frequently wanted than that of nickel.　The scheme for the separation of iron, aluminium, titanium, zinc, manganese, nickel, cobalt, magnesia and lime may be summarised (precipitates to left, solutions to right):—

Basic acetate separation (page 383)

Fe, Al, Ti (page 157)　　　　Zn, Mn, Ni, Co, Mg, Ca
　　　　　　　　　　　　(Formic acid and H_2S, page 385)

Zn (page 387)　　　　Mn, Ni, Co, Mg, Ca
　　　　　　　　(Ammonium sulphide, page 415)

Ni, Co, Mn　　　　Mg, Ca (page 200)
(Acetic acid and H_2S, page 416)

Ni, Co　　　　Mn (page 397)
(Potassium nitrite, page 416)

Co　　　　Ni

§ 200. The Properties of Cobalt and Nickel Sulphides.

Simultaneous Precipitation of Traces of Cobalt and Nickel with the Alumina and Iron.—The addition of ammonium chloride prevents, to a great extent, the precipitation of cobalt and nickel by ammonia; but if insufficient ammonium chloride be present, some nickel and cobalt may be carried down with the aluminium and iron hydroxides.　Baumhauer[2] determined the amounts of cobalt and nickel which were precipitated along with the iron when known mixtures of iron, cobalt and nickel were treated with the regular precipitating agents.　He found:

	Per cent. nickel.	Per cent. cobalt.
Ammonia (page 157)	27	48
Basic acetate process (page 383) . .	18	9
Barium carbonate in the cold (page 522) .	8	15

[1] S. W. Parr, *Journ. Amer. Chem. Soc.*, **19**, 341, 1897; S. R. Benedict, *ib.*, **26**, 695, 1904.
[2] E. H. von Baumhauer, *Zeit. anal. Chem.*, **10**, 217, 1871.　For the solubility of nickel ·hydroxide in ammonia, see W. Bonsdorff, *Zeit. anorg. Chem.*, **41**, 132, 1904.

But even when plenty of ammonium chloride is present, appreciable amounts may be precipitated with the iron and alumina as well as with the zinc. If these leakages are not guarded against by double precipitations,[1] the loss of cobalt and nickel, when precipitated at the end of a complex series of separations, may be quite serious.[2]

In the present case, the iron, aluminium and titanium are separated by the ammonia or the basic acetate process; the zinc as zinc sulphide; and finally the cobalt and nickel are precipitated as sulphides from a solution acidified with acetic acid. Manganese is not precipitated under these conditions. There is need for a few special remarks on the sulphides of nickel and cobalt.

Action of Ammonium Polysulphide on Nickel and Cobalt Salts.—These elements are not precipitated by hydrogen sulphide from solutions acidified with the mineral acids, but the sulphides are precipitated in the presence of acetic acid, particularly if ammonium or sodium acetate be present and the solution is warm. Ammonium sulphide precipitates the black or dark brown coloured sulphides from neutral or ammoniacal solutions of nickel and cobalt. The precipitate is but sparingly soluble in acetic acid and in very dilute hydrochloric acid. If yellow ammonium sulphide be used, that is, ammonium polysulphide, more or less nickel sulphide passes into solution and the filtrate will be coloured brown. It is generally supposed that either a soluble complex ammonium thionickelate, $(NH_4)_2NiS_{2+n}$, or a colloidal nickel persulphide is formed. The greater the excess of ammonium sulphide and the longer the solution is exposed to the air, the greater the tendency of the nickel to pass into solution in this manner.[3]

Action of Ammonium Monosulphide on Nickel Salts.—In the presence of ammonium hydroxide, colourless ammonium sulphide forms a violet-coloured solution with nickel salts in the cold. This soon becomes red and dark brown, and finally a black precipitate separates. On filtration, the filtrate appears colourless; but if the colourless solution be heated, a black precipitate of nickelous sulphide separates. Free ammonia is not necessary for the latter

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[1] T. Moore, *Chem. News*, 65, 75, 1892; A. Thomas, *ib.*, 35, 187, 1877; T. H. Laby, *ib.*, 89, 280, 1904; H. von Jüptner, *Oester. Zeit. Berg. Hütt.*, 41, 616, 1894. For clean separations with a large excess of ammonium chloride, see J. T. Dougherty, *Chem. News*, 95, 261, 268, 1907; V. Hassreidter, *Zeit. angew. Chem.*, 22, 1492, 1909. According to F. Ibbotson and H. Brearley (*Chem. News*, 81, 193, 1900), the nickel is adsorbed by the precipitated ferric hydroxide in the same way that filter-paper adsorbs salts from a solution; less nickel is adsorbed by increasing the amount of ammonium salt—chloride, nitrate or sulphate—in the solution, and decreasing the amount of ammonia. If, therefore, the precipitation of ferric hydroxide be made in presence of ammonium chloride, and so little ammonia that the filtrate is perceptibly acid, the separation of iron and nickel is a "good one." Schwarzberg's method of separation (P. Schwarzberg, *Liebig's Ann.*, 97, 216, 1856; J. F. W. Herschel, *Ann. Chim. Phys.*, (3), 49, 306, 1837) depends on the nice adjustment of the neutralisation so that the liquid loses its transparency without showing the least trace of a distinct precipitate, and fails to recover its clearness after standing some time; the solution is boiled, and the iron hydroxide is said to be precipitated comparatively free from nickel (R. Fresenius, *Quantitative Chemical Analysis*, London, 1, 437, 1876). For the adsorption of nickel salts by ferric hydroxide, see also M. Geloso and L. S. Lévy, *Compt. rend.*, 189, 175, 1929; L. S. Lévy, *ib.*, 189, 426, 1929.

[2] According to H. Remmler (*Zeit. anorg. Chem.*, 2, 221, 1892), cobalt hydroxide which has been precipitated by ammonia and washed, slowly redissolves when allowed to stand in contact with ammonia. E. Donath (*Monats.*, 14, 93, 1893) says that the deep blue liquid obtained by the action of concentrated potash on cobaltous hydroxide is a solution of the oxide in the lye.

[3] A. Lecrenier, *Chem. Ztg.*, 13, 436, 449, 1889; R. Fresenius, *Journ. prakt. Chem.*, (1), 82, 257, 1861; A. Villiers, *Compt. rend.*, 119, 1208, 1263, 1894; P. de Clermont, *ib.*, 117, 229, 1893; G. Chesneau, *ib.*, 123, 1068, 1896; U. Anthony and G. Magri, *Gazz. Chim. Ital.*, 31, (2), 265, 1901; F. Stolba, *Journ. prakt. Chem.*, (1), 96, 53, 1866; A. Villiers, *Bull. Soc. chim.*, (3), 13, 165, 1895.

action. Colourless ammonium sulphide, free from the polysulphide, precipitates nickel completely as sulphide, and the filtrate, in the absence of air, will be free from nickel and colourless. However, ammonium monosulphide rapidly oxidises to polysulphide when exposed to the air, and it is almost impossible to prevent some nickel passing into the filtrate, particularly when working with large quantities of this metal. It is useless to try and get the brown solution clear by filtration. The best method of dealing with the coloured filtrate is to coagulate the nickel sulphide by the addition of ammonium chloride, followed by 5 or 10 minutes' boiling; re-filtration is then generally successful. These troubles are alleviated by passing hydrogen sulphide into the warm ammoniacal solution.

Action of Acids upon Nickel and Cobalt Sulphides.—These sulphides, once formed, are generally said to be insoluble in acetic and hydrochloric acids. The alleged "insolubility" is a misnomer, because relatively large amounts of the freshly precipitated sulphides do dissolve in dilute hydrochloric acid—1 volume acid, sp. gr. 1·12, with 5 volumes of water.[1] The reverse action, the precipitation of the sulphides in acid solution by hydrogen sulphide, is exceedingly slow. If over a trace of acetic or hydrochloric acid be present, neither sulphide will be precipitated in the cold; but if the solution be hot, both nickel and cobalt sulphides will be precipitated in the presence of ammonium or sodium acetate. Cobalt and nickel sulphides become "insoluble" in these acids on standing for some time, or on heating. They then require digesting with aqua regia for their solution.[2]

According to Thiel and Gessner,[3] nickel sulphide exists in three different forms. The α-modification is dissolved by mineral acids down to 0·01N-concentration and is easily oxidised; glacial acetic acid rapidly and water slowly convert it into the β-variety, soluble in hot 2N-HCl. The γ-modification is soluble only with the aid of oxidising agents. The two latter varieties—β and γ—are formed chiefly by precipitation from very dilute solutions; but the γ-variety also separates from hot concentrated solutions. All three forms are produced under the ordinary conditions of analysis. The reduced solubility acquired by fresh precipitates on exposure to air is due to the oxidation of the sulphide to sparingly soluble compounds and the conversion of these by the excess of hydrogen sulphide to the β- and γ-varieties. All these sulphides are polymers; the α-variety is amorphous and the other two crystallise in different forms.

§ 201. The Separation of Manganese from Cobalt and Nickel.

Precipitation of Nickel, Cobalt and Manganese Sulphides.[4]—The filtrate from the zinc sulphide is neutralised with ammonia and an excess of ammonia (free from carbonate) is added to the solution. Hydrogen sulphide is passed through the warm (70°–80°) solution, whereby the mixed sulphides of manganese, cobalt and nickel [5] are precipitated. The alkalies and alkaline earths remain in

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[1] H. Baubigny, *Compt. rend.*, 94, 963, 1183, 1251, 1417, 1473, 1715, 1882; 95, 35, 1882; 105, 751, 806, 1887; 106, 132, 1888; *Chem. News*, 57, 55, 1888.

[2] W. Ostwald, *Die wissenschaftlichen Grundlagen der analytischen Chemie*, Leipzig, 145, 1894; London, 149, 1895; J. L. R. Morgan, *Journ. Amer. Chem. Soc.*, 21, 494, 1899; W. Herz, *Zeit. anorg. Chem.*, 27, 390, 1901; 28, 342, 1901.

[3] A. Thiel and H. Gessner, *Zeit. anorg. Chem.*, 86, 1, 1914; *Chem. Zentr.*, i, 18, 1914.

[4] R. Fresenius, *Anleitung zur quantitativen Analyse*, Braunschweig, 1, 579, 1875; London, 1, 429, 1876; O. Hackl, *Chem. Ztg.*, 46, 385, 1922.

[5] Also copper, if present.

solution. Filter at once,[1] using a fine grade filter-paper and wash with water containing a little ammonium sulphide and chloride in solution.

The filtrate may come through brown. In any case—clear or brown—evaporate the filtrate to about 50 c.c.; add freshly prepared ammonium sulphide; acidify with acetic acid; and boil for some time. This will curdle the sulphides not retained on the filter-paper and allow them to be readily removed by filtration. The danger of losing nickel and cobalt sulphides is here so serious that, if any metal escaped with the first filtrate, it is advisable to test the filtrate again to make sure that all the cobalt and nickel have been precipitated.

Separation of Nickel and Cobalt Sulphides.—The washed precipitate is dissolved in aqua regia and boiled to expel the excess of acid. Add excess of sodium carbonate to the solution and then acetic acid [2] until the solution is faintly acid. Add 3 to 5 grms. of sodium or ammonium acetate [3]; dilute the solution to, say, 200 c.c.; pass hydrogen sulphide through the warm solution (70°–80°). The sulphides of cobalt and nickel [4] are precipitated, the manganese remains in solution. Filter at once through a close-packed filter-paper and wash with hydrochloric acid (sp. gr. 1·025) saturated with hydrogen sulphide in order to remove any manganese sulphide precipitated with the cobalt and nickel sulphides.

The risk of losing cobalt and particularly nickel, is here very great. Hence make sure that the precipitation is complete by evaporating the clear filtrate to 50 c.c., adding an excess of ammonium sulphide, acidifying with an excess of acetic acid and warming the solution. If nickel or cobalt be present, a precipitate will be formed. Filter. Test the filtrate as before. When all the cobalt and nickel have been precipitated, wash as before.[5]

Dry the filter-paper and contents. Incinerate to burn off the paper. Dissolve the precipitate in hydrochloric acid, mixed with a little nitric acid, and determine the nickel and cobalt separately as indicated below.

§ 202. The Separation of Cobalt and Nickel— Fischer's Nitrite Process.

Fischer's process [6] depends on the formation of an "insoluble" potassium cobaltinitrite—Fischer's salt—under conditions where the corresponding

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[1] All sulphides precipitated from hot solutions should be filtered and washed at once, so as to prevent oxidation. S. P. Sharples, *Amer. J. Science*, (2), **50**, 248, 1870; *Chem. News*, **22**, 259, 1870.

[2] W. Funk (*Zeit. anal. Chem.*, **45**, 562, 1906) uses formic acid.

[3] Say 5 grms. of ammonium acetate per gram of cobalt/nickel. H. Kâto (*Journ. Chem. Soc. Japan*, **55**, 337, 1934) adds sodium acetate to the acetic acid solution until the acidity lies between p_H 4·0 and 4·8.

[4] Also copper, zinc and uranium, if present. W. Gibbs, *Amer. J. Science*, (2), **39**, 62, 1865; *Chem. News*, **11**, 147, 1865.

[5] The manganese in the filtrate from the nickel and cobalt sulphides is determined as indicated on page 397.

[6] *Cf.* page 608. A. Duflos and N. W. Fischer, *Pogg. Ann.*, **72**, 475, 1847; **74**, 115, 1849; H. Rose, *ib.*, **110**, 411, 1860; A. Stromeyer, *Liebig's Ann.*, **96**, 218, 1855; W. Gibbs and F. A. Genth, *ib.*, **104**, 309, 1857; *Chem. News*, **28**, 51, 1873; H. Baubigny, *Ann. Chim. Phys.*, (6), **17**, 103, 1889; F. Gauhe, *Zeit. anal. Chem.*, **4**, 56, 1865; **5**, 74, 1866; A. Brauner, *ib.*, **16**, 195, 1877; O. Brunck, *Zeit. angew. Chem.*, **20**, 834, 1847, 1907; H. Herrenschmidt and E. Capelle, *Le Cobalt et le Nickel*, Rouen, 1888; *Chem. News*, **69**, 112, 128, 142, 1894; *Zeit. anal. Chem.*, **32**, 607, 1893; W. Funk, *ib.*, **46**, 1, 1907; E. A. Hadow, *Chem. News*, **3**, 85, 1860; G. Ferreri, *Giorn. Chim. Ind. Appl.*, **5**, 339, 1923; F. G. Germuth, *Chemist-Analyst*, **19**, 4, 1930; L. Bertiaux, *Ann. Chim. anal.*, **18**, 377, 1913; A. A. Vassiliev, *Zeit. anal. Chem.*, **78**, 439, 1929.

nickel salt is soluble. It is said that the presence of two parts of cobalt per million can be detected in this way.

Precipitation of Potassium Cobaltinitrite.—Evaporate the solution containing the mixed cobalt and nickel salts to dryness. Take up the residue with one or two drops of concentrated hydrochloric acid and as little water as possible. Add caustic potash[1] to the solution until no more precipitate is formed on adding another drop of alkali. The solution will then have an alkaline reaction. Acidify the solution with an excess of acetic acid.[2] Suppose that the total volume is between 5 and 10 c.c. Add half this volume of a 50 per cent. solution of potassium nitrite[3] and stir the solution vigorously. Let the solution stand for 24 hours in a warm place. Test if the precipitation is complete by pipetting off a little of the clear solution and adding a little more potassium nitrite. If precipitation be not complete, transfer the small portion back to the main solution and repeat the treatment with more potassium nitrite solution.

Filter the solution containing the yellow crystalline precipitate.[4] Use the clear filtrate for transferring the precipitate to the filter-paper. Wash the precipitate with a barely acid 5 per cent. solution of potassium nitrite[5] until 1 c.c. of the washings boiled with hydrochloric acid and treated with caustic potash and bromine gives no black precipitate of nickel hydroxide, or until a portion of the washings neutralised with ammonia is not coloured brown with ammonium sulphide.

Precipitation of Cobalt Hydroxide.—Transfer the precipitated potassium cobaltinitrite[6] to a porcelain dish, cover with a clock-glass and add hydrochloric acid until no more nitric oxide is evolved, showing that the nitrite is decomposed. Rinse the under side of the clock-glass into the dish and treat the solution with an excess of caustic potash and bromine,[7] taking care that

[1] Some of the very best grades of caustic alkali contain nickel derived from the dishes in which the alkalies were made. Iron, alumina and silica also appear in all but the very best grades of caustic alkali.

[2] L. L. de Koninck (*Bull. Soc. chim. Belg.*, 23, 11, 200, 1909) considers that the subsequent precipitation is more complete if the solution contains a little free nitric acid and more potassium nitrite is added than suffices to neutralise the nitric acid.

[3] POTASSIUM NITRITE SOLUTION.— 1 grm. of the salt per 2 c.c. of water, and just neutralise the solution with acetic acid. The solution is prepared for use as required. If the solution has any flecks of insoluble alumina or silica, filter. Always test each batch of potassium nitrite for silica, alumina and lead before it is used.

[4] If alkaline earths, copper or lead be present, some nickel may be precipitated with the cobalt owing to the formation of triple nitrites of potassium, nickel and the third element. It is also important to use freshly prepared ammonium sulphide, or ammonia free from carbonates, in separating the alkaline earths from the ammonium sulphide group—H. Baubigny, *Compt. rend.*, 107, 1148, 1888. Zinc and cadmium do not give precipitates when treated by the nitrite process.

[5] Some recommend washing with a 10 per cent. solution of potassium acetate containing a little potassium nitrite, because the potassium acetate can be removed by washing with alcohol, in which it is fairly soluble, while potassium nitrite is but sparingly soluble in this solvent. B. Brauner, *Zeit. anal. Chem.*, 16, 195, 1877. There is no need for the alcohol washing here, and potassium nitrite alone gives better results.

[6] O. L. Erdmann, *Journ. prakt. Chem.*, (1), 97, 397, 1866; M. St Evre, *ib.*, (1), 54, 84, 1851; *Compt. rend.*, 33, 166, 1851; A. Remelé, *Zeit. anal. Chem.*, 3, 313, 1864; W. Braun, *ib.*, 6, 72, 1867; 7, 313, 1868; A. Rosenheim and I. Koppel, *Zeit. anorg. Chem.*, 17, 35, 1898; R. Wegscheider, *ib.*, 49, 441, 1906; T. Rosenbladt, *Ber.*, 19, 2535, 1886; S. P. Sadtler, *Amer. J. Science*, (2), 49, 189, 1870; *Chem. News*, 22, 8, 15, 26, 1870; W. Blomstrand, *Chemie der Jetztzeit*, Heidelberg, 414, 1869.

[7] L. Dede (*Chem. Ztg.*, 35, 1077, 1911) recommends sodium or potassium persulphate in place of bromine, since only enough alkali is then needed to ensure alkalinity after the addition of the persulphate. The precipitation occurs in the cold after standing one or two hours with frequent shaking. It is claimed that the precipitated cobalt (or nickel) hydroxide can be easily washed.

the solution is kept alkaline with potash.   The cobalt is precipitated as black
cobalt hydroxide. First wash by decantation with hot water, then filter through
a close-packed filter-paper.   After transferring the whole of the precipitate
to the filter-paper, wash thoroughly with hot water until the washings are free
from alkali.   Dry and ignite the filter-paper and precipitate in a Rose's
crucible.   Cool, then ignite the contents of the crucible in a stream of hydrogen
and weigh as metallic cobalt.[1]

Purification from Silica.—Owing to the large amount of alkali used in these
determinations, the precipitates are particularly liable to contamination with
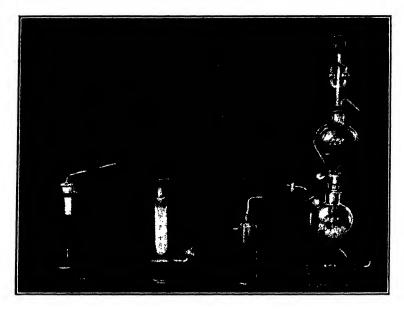
FIG. 98.—Reduction of Cobalt Oxide.

silica and alumina from the glass and porcelain vessels.   To remove the silica,
treat the oxide with hydrochloric acid in a porcelain crucible; evaporate the
mass to dryness; mix with concentrated hydrochloric and nitric acids; add
hot water; filter; wash with hot water; ignite the paper and contents; and
weigh as silica—SiO_2.

Ignition in a Rose's Crucible.—Rose's crucible [2] has an opening in the lid for
the introduction of an earthenware pipe *A* for leading gas into the red-hot
crucible.[3]   The arrangement for this particular experiment is indicated in

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[1] T. Bayley, *Chem. News*, 34, 81, 1876; A. Carnot, *ib.*, 59, 183, 1889; *Compt. rend.*, 108,
741, 1889; B. Brauner, *Zeit. anal. Chem.*, 16, 195, 1877.

[2] H. Rose, *Pogg. Ann.*, 110, 128, 1860.   In the absence of a Rose's crucible, an ordinary
crucible and a common clay pipe of such a size that the mouth of the inverted bowl will just
pass into the crucible may be used.   A glazed crucible is preferable when a correction is
subsequently made for silica.   E. Murmann (*Monats.*, 19, 403, 1898) describes a Gooch
crucible with a tubulure below the perforated base whereby the precipitate can be filtered
as in a Gooch crucible, and subsequently heated in a current of any desired gas.   The tubes
are easily broken, and they are therefore expensive.

[3] W. Gibbs (*Chem. News*, 28, 30, 1873; R. H. Lee, *ib.*, 24, 234, 1871; *Amer. J. Science*,
(3), 2, 44, 1871) recommends a circular disc of porous earthenware above the substance to be
heated and below the gas inlet pipe.   The gases pass through the disc to the substance to be
reduced by diffusion.   Mechanical loss is thus prevented.   The "soft" porous capsule can
be easily filed to fit the crucible perfectly.

fig. 98. The hydrogen [1] is generated in a Kipp's apparatus, *B.* The hydrogen should be freed from arsenic, antimony, phosphorus and carbon compounds by washing in a solution, *C,* of potassium permanganate in concentrated sulphuric acid; from sulphur compounds by washing in a concentrated solution of caustic soda, *D;* and dried by passing through a tower of calcium chloride, *E.* [2] Explosions may be prevented by placing a glass tube containing cotton-wool between discs of wire gauze immediately after the drying tower. [3]

The Rose's crucible is placed in position and, when the air has been expelled by the hydrogen generated in the Kipp's apparatus, light the burner and gradually raise the temperature of the crucible and contents to bright redness. [4] The current of gas [5] should be so regulated that from about two to four bubbles per second pass through the wash-bottle during the earlier stages of the reduction, when comparatively large volumes of steam are being evolved. The velocity of the stream may then be increased to about eight bubbles per second. In about 10 or 15 minutes the oxide should all be reduced to metal. Remove the flame and let the crucible cool in the current of gas. Place the crucible in a desiccator and, when cold, weigh as metallic cobalt. For example the following figures were obtained:

Rose's crucible plus metal	15·3572 grms.
Rose's crucible alone	14·8731 grms.
Metallic cobalt	0·4841 grm.

The reduction is necessary because oxides of varying degrees of oxidation are formed by the ignition in air. Some prefer to convert the oxides into sulphates before weighing, and thus avoid the reduction. [6] (See § 208, p. 425.)

Determination of Nickel.—The nickel is determined [7] in the filtrate from the cobalt by acidifying the solution with hydrochloric acid in order to decompose the nitrite. Precipitate the black nickel hydroxide, $Ni(OH)_3$, by adding caustic potash and bromine as just indicated for cobalt. [8] The precipitate, after washing, is reduced to the metallic state in a Rose's crucible, as described for cobalt, or it may be ignited in an ordinary crucible and weighed as nickel oxide—NiO. [9]

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[1] Not coal gas, because of the formation of cobalt carbides.

[2] E. Schobig, *Journ. prakt. Chem.*, (2), 14, 289, 1876; E. Varenne and E. Hebre, *Bull. Soc. chim.*, (3), 28, 523, 1902.

[3] R. Fresenius, *Zeit. anal. Chem.*, 12, 73, 1873; C. G. Hopkins, *Journ. Amer. Chem. Soc.*, 21, 645, 1899; *Chem. News*, 81, 134, 1900.

[4] The reduction of cobalt oxide begins at about 132° (W. Müller, *Pogg. Ann.*, 136, 51, 1869); it is rapid at temperatures exceeding 500° and is complete at temperatures between 960° and 1000° (H. T. Kalmus, *Journ. Ind. Eng. Chem.*, 6, 107, 1914).

[5] J. Habermann (*Zeit. anal. Chem.*, 28, 88, 1889) recommends an alloy of tin with 83–84 per cent. of zinc in preference to zinc alone. The form of Habermann's alloy remains the same after the zinc has dissolved, and in consequence none falls into the lower bulb of the Kipp's generator.

[6] E. J. Maumené, *Compt. rend.*, 79, 179, 1874; F. Gauhe, *Zeit. anal. Chem.*, 4, 53, 1865; W. J. Russell, *Journ. Chem. Soc.*, 16, 51, 1863; H. H. Willard and D. Hall (*Journ. Amer. Chem. Soc.*, 44, 2226, 1922) say that ignition of the sulphate at 550° is the most accurate method of all. R. Cernatesco and E. Vascautanu (*Ann. Sci. Univ. Jasssy*, 15, 69, 1928) claim that, on ignition in a current of oxygen in a Rose's crucible, conversion to Co_3O_4 is complete.

[7] The electrolytic process, page 423, may be used, and in fact is strongly recommended, if convenient.

[8] If the bromine be omitted, the apple-green precipitate of nickel hydroxide—$Ni(OH)_2$—is difficult to filter and to wash free from alkali.

[9] It is very difficult to wash the precipitate free from alkali. Alternatively the acid solution can be treated with ammonium sulphide and the precipitate ignited and weighed as NiO or metal. Silica can be determined as indicated in the text for cobalt.

The potassium nitrite process is by no means perfect, since nickel can be afterwards detected with the cobalt, and cobalt with the nickel. The error in the determination of the cobalt is, however, almost balanced by the slight solubility of the potassium cobaltinitrite precipitate in the mother liquid. The precipitate should not be allowed to stand much over the 24 hours without attention. This process, as indicated above (and also Liebig's cyanide process), breaks down if alkaline earths be present.

§ 203. The Separation of Nickel—Liebig's Cyanide Process.

This process is based on the fact that nickel hydroxide alone is precipitated by bromine from an alkaline solution containing an excess of potassium cyanide. The nickel probably occurs in solution as a double cyanide of nickel and potassium, whereas the cobalt occurs in solution as potassium cobalticyanide. Bromine reacts with the former, not with the latter.[1]

The solution of the mixed sulphides is neutralised with potassium hydroxide and treated with a solution of "pure" potassium cyanide until the precipitate first formed redissolves; add more potassium cyanide—in all, 3 or 4 grms. usually suffice. Then about 5 grms. of potassium hydroxide are added and about 5 c.c. of bromine, with constant stirring, until the nickel is all precipitated. If necessary, add more potash in order to keep the solution alkaline throughout the whole process, or the precipitation will not be complete. The nickel should all be precipitated in about an hour. Dilute with about 800 c.c. of cold water and determine the nickel as indicated above.[2]

The filtrate, containing the cobalt as potassium cobalticyanide, is evaporated to dryness with dilute sulphuric acid in a platinum dish on a water bath in a fume cupboard; then add concentrated sulphuric acid and evaporate on a sand bath until dense white fumes are evolved and effervescence has ceased. This shows that the colourless cobalticyanide is all changed to rose-red cobalt sulphate. Cool. Dissolve the residue in water and precipitate the cobalt with bromine in alkaline solution as indicated above.

In special cases, certain other methods for the determination of cobalt and nickel are useful. If suitable apparatus be available, the electrolytic methods of separation are splendid. The following are also useful in special cases.

§ 204. The Separation of Small Amounts of Cobalt from Large Amounts of Nickel—Ilinsky and Knorre's α-Nitroso-β-naphthol Process.

This process[3] depends on the fact that a solution of α-nitroso-β-naphthol precipitates cobalt from a mixed solution of cobalt and nickel. The reagent

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[1] J. von Liebig, *Liebig's Ann.*, 65, 244, 1848; 87, 128, 1853; F. Wöhler, *ib.*, 70, 256, 1849; F. Gauhe, *Zeit. anal. Chem.*, 5, 75, 1866; C. Krauss, *ib.*, 30, 227, 1891; *Chem. News.* 63, 254, 264, 280, 293, 1891; W. Gibbs, *ib.*, 11, 125, 1865; *Amer. J. Science*, (2), 39, 58, 1865; E. A. Hadow, *Chem. News*, 3, 85, 1860; H. Fleck, *Journ. prakt. Chem.*, (1), 97, 303, 1866; F. J. Hambly, *Chem. News*, 65, 299, 1892; H. König, *Chem. Ztg.*, 37, 1106, 1913.

[2] Or use the electrolytic process, page 423, which gives better results than the process indicated in the text.

[3] M. Ilinsky and G. von Knorre, *Ber.*, 18, 699, 2728, 1885; 20, 283, 1887; *Chem. News*, 52, 301, 1885; C. Krauss, *Zeit. anal. Chem.*, 30, 227, 1891; L. L. de Koninck, *Rev. Univ. Mines*, 9, 243, 1890; *Chem. News*, 62, 19, 1890; C. Meineke, *Zeit. angew. Chem.*, 1, 3, 1888; G. von. Knorre, *ib.*, 6, 264, 1893; R. Burgess, *ib.*, 9, 596, 1896; M. Ilinsky, *Chem. Ztg.*, 19, 1421, 1895; H. Copaux, *Bull. Soc. chim.*, (3), 29, 301, 1903; *Chem. News*, 87, 291, 1903; G. Slawik, *Chem. Ztg.*, 38, 514, 1914; A. Eder, *ib.*, 46, 430, 1922; K. Wagenmann, *Metall*

is so sensitive that a visible turbidity is produced in solutions which give no sign of cobalt by the nitrite process. The precipitate is rather bulky, so that the process is most convenient for separating small quantities of cobalt from comparatively large amounts of nickel.

Digest the mixed sulphides with concentrated hydrochloric acid and add just sufficient concentrated nitric acid, drop by drop, to effect solution. Evaporate to dryness to expel the excess of nitric acid, adding more hydrochloric acid if necessary. Add a few drops of hydrochloric acid to the residue, take up in water and filter off any sulphur which may have separated out. Dilute the solution so that it contains not more than about 0·1 grm. of cobalt per 100 c.c. Heat to boiling and add a hot, freshly prepared solution of α-nitroso-β-naphthol [1] at the rate of 100 c.c. for each 0·1 grm. of cobalt in solution. Heat for a few minutes, stirring well. Stand for 2 hours, filter, wash with water. Dry, ignite in a current of oxygen and weigh as Co_3O_4, or reduce the oxide in hydrogen and weigh as metal.[2]

The greatest difficulty in this process is the elimination of carbon. The cobalt seems to form a compound with carbon which is not destroyed even by ignition over a blast. The best procedure is to evaporate the washed precipitate to dryness with concentrated sulphuric acid, ignite in an air-bath at 400° to 500° and weigh as $CoSO_4$. Ilinsky and Knorre's reagent also precipitates copper and iron quantitatively, and bismuth, chromium, silver and tin in part. It does not precipitate aluminium, lead, cadmium, manganese, nickel, mercury, arsenic, antimony, calcium, magnesium and the alkali metals, although these constituents may be carried down mechanically with the cobalt precipitate. The latter must then be purified by solution and reprecipitation.

§ 205. The Separation of Small Amounts of Nickel from Large Amounts of Cobalt—Brunck's Dimethylglyoxime Process.

Reference has already been made (page 412) to Tschugajeff's test. When small quantities of nickel are in question, the solution should be evaporated almost to dryness.[3] The rose coloration is best seen when the solution is filtered

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und Erz, **18**, 447, 1921; J. E. Clennell, *Mining Mag.*, **36**, 270, 1927; W. J. Agnew, *Analyst*, **53**, 31, 1928; C. Mayr and F Feigl, *Zeit. anal. Chem.*, **90**, 15, 1932; L. A. Congdon and T. H. Chen, *Chem. News*, **128**, 132, 1924; L. Philippot, *Bull. Soc. chim. Belg.*, **44**, 140, 1935; A. Craig and L. Culdroff, *Chemist-Analyst*, **24**, 10, 1935; F. G. Germuth, *ib.*, **19**, 4, 1930. For the use of α-nitro-β-naphthol as a precipitant instead of α-nitroso-β-naphthol, see C. Mayr, *Zeit. anal. Chem.*, **98**, 402, 1934.

[1] α-NITROSO-β-NAPHTHOL SOLUTION.—Dissolve 2 grms. of the solid in 75 c.c. of cold glacial acetic acid. Dilute with 75 c.c. of water. Filter. The solution does not keep very well.

[2] The nickel can be determined in the filtrate by evaporating to a small bulk with sulphuric acid and expelling most of the acid on a sand bath. The nickel may then be precipitated with caustic potash and bromine water as indicated above.

[3] L. Tschugajeff, *Ber.*, **38**, 2520, 1905; K. Kraut, *Zeit. angew. Chem.*, **19**, 1793, 1906; O. Brunck, *ib.*, **20**, 834, 1844, 1907; *ib.*, **27**, 315, 1914; *Chem. News*, **99**, 275, 1909; A. Ivanicki, *Stahl Eisen*, **27**, 358, 1908; H. Wdowiszewski, *ib.*, **27**, 960, 1908; **29**, 358, 1910; P. Bogoluboff, *ib.*, **30**, 458, 1911; L. V. W. Spring, *Journ. Ind. Eng. Chem.*, **3**, 255, 1911; F. Ibbotson, *Chem. News*, **104**, 224, 1911; H. Pederson, *Met.*, **8**, 335, 1911; S. W. Parr and J. M. Lindgren, *Trans. Amer. Brassfounders' Assoc.*, **5**, 120, 1912; S. Zinberg, *Zeit. anal. Chem.*, **52**, 529, 1913; H. König, *Chem. Ztg.*, **37**, 1106, 1913; R. Belasio and M. Marchionneschi, *Ann. Chim. appl. Ital.*, **1**, 133, 1914; W. J. Marsh, *Journ. Phys. Chem.*, **18**, 705, 1914; R. Riedel, *Elektrochem. Zeit.*, **21**, 5, 1915; T. L. Walker, *Trans. Roy. Soc. Canada*, **9**, 93, 1915; C. A. Knittel, *Metal Ind.*, **14**, 77, 1916; K. Wagenmann, *Ferrum*, **12**, 126, 1915; P. Covitz, *Met. Chem. Eng.*, **15**, 682, 1916; S. Rothschild, *Chem. Ztg.*, **41**, 29, 1917; H. Grossmann and J. Mannheim, *Zeit. angew. Chem.*, **30**, (1), 159, 1917; P. Nicolardot and G. Gourmain, *Bull. Soc. chim.*, (4), **25**,

and the precipitate shaken with water.[1] Larger amounts of nickel give a scarlet-red precipitate. If the precipitate be dissolved in a mixture of chloroform and alcohol, and the solution evaporated to dryness, red needles of nickel-α-dimethylglyoxime are formed.[2] The reaction is applied quantitatively as follows: —

Evaporate the solution of mixed sulphides to dryness on a water bath. Dilute the residue to about 300 or 500 c.c., such that the cobalt is less concentrated than 0·1 grm. per 100 c.c. Warm the solution to about 50°; add 0·2 grm. of dimethylglyoxime in alcoholic solution [3] and then add about 2 grms. of sodium acetate.[4] Stir the solution thoroughly and let it stand about an hour. A voluminous precipitate of the nickel oxime separates.[5] Filter the solution through an asbestos-packed Gooch crucible. Wash with warm water (50°), and dry for about an hour at 110°–120°, after which there should be no further loss on drying.[6] When cold, weigh the mass as $C_8H_{14}N_4O_4Ni$,

338, 1919; G. T. Prior, *Min. Mag.*, 18, 349, 1919; G. E. F. Lundell and J. I. Hoffman, *Journ. Ind. Eng. Chem.*, 13, 540, 1921; H. Rubricus, *Chem. Ztg.*, 46, 26, 1922; R. Strebinger and I. Pollak, *Mikrochem.*, 2, 125, 1924; I. Pollak, *ib.*, 2, 17, 1924; L. A. Congdon and C. H. Belge, *Chem. News*, 128, 67, 1924; P. Wenger and E. Rogovine, *Helv. Chim. Acta*, 10, 242, 1927; C. L. Thomas, *Journ. Elisha Mitchell Sci. Soc.*, 43, 214, 1928; G. W. Kühl, *Chem. Ztg.*, 53, 279, 1929; G. I. Smirnov, *Uchenuie Zapiski Kazan Gosudarst Univ.*, 90, 1025, 1930; F. Feigl and H. J. Kapulitzas, *Zeit. anal. Chem.*, 82, 417, 1930; T. Nagai, *Complete Abs. Japan. Chem. Lit.*, 6, 409, 1932; P. S. Brown, *Metal Ind.*, 5, 349, 1913; E. P. Later, *Foundry*, 41, 243, 1913; L. C. Merriam, *Chemist-Analyst*, 22, 8, 1917; F. G. Germuth, *ib.*, 19, 4, 1930; L. Dufty, *Journ. Iron Steel Inst.*, 90, 52, 1914; S. Ishimaru, *Journ. Chem. Soc. Japan*, 54, 367, 1933; A. Guédras, *Aciers spéciaux*, 8, 373, 1933; J. Ranedo, *Anal. Fis. Quim.*, 32, 611, 1934; R. D. Midson, *Chem. Eng. Min. Rev.*, 29, 196, 1937; G. Batz, *Zeit. anorg. allgem. Chem.*, 231, 15, 1937; N. S. Krupenio, *Zavodskaya Lab.*, 6, 239, 1937; E. Azzarello, A. Accado and F. Abramo, *Atti V. Congr. Nazl. Chim. Pura Applicata*, 1935, (2), 658, 1936; G. Spacu and C. G. Macarovici, *Bul. Soc. Stiinti Cluj*, 8, 444, 1936. For the determination of small quantities of nickel in rock analysis, see H. F. Harwood and L. S. Theobald, *Analyst*, 58, 673, 1933. For the colorimetric determination of nickel *via* dimethylglyoxime, see A. P. Rollet, *Compt. rend.*, 183, 212, 1926; B. S. Evans, *Analyst*, 58, 450, 1933. For the separation of nickel and palladium, see M. Wunder and V. Thuringer, *Ann. Chim. anal.*, 17, 201, 1912. Platinum is qualitatively, not quantitatively, precipitated—M. Wunder and V. Thuringer, *ib.*, 17, 328, 1912.

[1] It should be noted that ferrous salts also give a red colour with dimethylglyoxime, but no precipitate.—W. Vaubel, *Zeit. öffent. Chem.*, 27, 163, 1921; E. J. Kraus, *Zeit. anal. Chem.*, 71, 189, 1927. For the detection of nickel by glyoxime and for the increased sensitivity of the test, see A. R. Middleton and H. L. Miller, *Journ. Amer. Chem. Soc.*, 38, 1280, 1916; M. Matsui and T. Nakazawa, *Mem. Coll. Sci. Kyoto*, 4, 265, 1920; O. Häckl, *Chem. Ztg.*, 46, 385, 1922; F. Kirschner, *Mikrochem.*, 1, 88, 1923; F. Feigl, *Ber.*, 57B, 758, 1924; P. Agostini, *Ann. Chim. appl.*, 19, 164, 1929; G. Sensi and R. Testori, *ib.*, 19, 383, 1929; E. C. Righellato, *Chem. Age*, 28, 574, 1933.

[2] H. Grossmann and B. Schück (*Chem. Ztg.*, 31, 535, 643, 911, 1907) detect nickel in similar circumstances by means of dicyanodiamidine sulphate. The process is also used quantitatively—H. Grossmann, B. Schück, and W. Heilborn, *Bull. Soc. Ind. Rouen*, 38, 116, 125, 1910; P. Nicolardot and G. Gourmain, *Bull. Soc. chim.*, (4), 25, 338, 1919.

[3] DIMETHYLGLYOXIME SOLUTION. — Dissolve 0·2 grm. of α-dimethylglyoxime— $CH_3.C:NOH.C:NOH.CH_3$—in 20 c.c. of 98 per cent. alcohol. Filter the solution if necessary. The solution will not keep very long.

[4] The precipitate is soluble in free mineral acids. Ammonium and sodium acetates render the mineral acids inert.

[5] The solution should not contain more than half its volume of the alcoholic dimethylglyoxime, or appreciable amounts of the nickel oxime may be dissolved. Otherwise an excess of the solution does no harm. Theoretically, four times as much dimethylglyoxime by weight is needed as nickel to be precipitated. A small excess suffices—say five times; but if much cobalt be present, a greater excess is needed, owing to some of the glyoxime forming a complex salt with the cobalt.

[6] P. Bogoluboff, *Stahl Eisen*, 29, 458, 1910. P. Nuka (*Zeit. anal. Chem.*, 91, 29, 1932) says that the precipitate should stand for an hour before filtering, and then be washed with cold water to reduce solubility losses.

and multiply the weight so obtained by 0·2586 to get the corresponding amount of nickel oxide, NiO. There is no danger of loss of nickel if the precipitate be heated below 250°.[1] At this temperature the salt begins to sublime undecomposed.

The process can be used for separating nickel from zinc, manganese, iron, cobalt, aluminium and chromium in ammoniacal solutions in the presence of sodium acetate.[2] With zinc-nickel mixtures, for example, the dimethylglyoxime is destroyed by boiling the filtrate from the nickel with hydrochloric acid, and the zinc precipitated by Tamm's process.

§ 206. Atack's α-Benziloxime Process.

Atack[3] gets excellent results with α-benziloxime in alcoholic solution to which a little ammonia has been added. The warm reagent is added to a solution of the nickel salt, made alkaline with ammonia, and the whole heated on a water bath until the precipitate has coagulated. After about an hour, the precipitate is collected on a tared filter-paper or Gooch crucible, washed with warm 50 per cent. alcohol, then with hot water, dried at 110° and weighed. The precipitate contains 13·91 per cent. of nickel oxide, NiO. Nitrates interfere. The interference of cobalt and ferric iron is prevented by the addition of sodium citrate; of zinc and magnesium,· by ammonium chloride; of manganese, by a slight excess of acetic acid or citric acid and hydrazine, to prevent oxidation of the manganese; of chromium, by ammonium tartrate; and of copper, by Rochelle salt.

§ 207. The Electrolytic Process for Cobalt and Nickel— Fresenius and Bergmann's Process.

Nickel and cobalt cannot be separated satisfactorily from solutions containing free acids, but they are readily separated from solutions of the double cyanides, double oxalates and double sulphates, or in the presence of alkali

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[1] According to Ibbotson (l.c.), the precipitate can be washed with ammonium nitrate solution and ignited to nickel oxide. The cobalt can be determined in the filtrate by evaporating it to a small bulk and proceeding as indicated above. Brunck recommends the joint determination of cobalt and nickel, direct determination of nickel, and cobalt by difference.

[2] If iron, aluminium or chromium is present, tartaric acid is added to prevent the precipitation of hydroxides on adding ammonia. When a solution of ferric and cobalt salts is made ammoniacal, an insoluble iron-cobalt complex is precipitated, but with iron in the ferrous state no precipitate is formed. Hence if iron be present, it is necessary to keep it in the ferrous condition by the addition of, say, sulphurous acid. Dimethylglyoxime then precipitates nickel quantitatively, while iron and cobalt remain in solution. When chromium is also present, some ammonium chloride is added—O. Brunck, *Zeit. angew. Chem.*, 27, 315, 1914; J. G. Weeldenburg, *Chem. Weekblad*, 21, 358, 1924; *Rec. Trav. chim.*, 43, 465, 1924.

[3] F. W. Atack, *Analyst*, 38, 316, 1913; *Journ. Chem. Soc.*, 104, 730, 1913; *Chem. Ztg.*, 37, 773, 1913; H. Grossmann and J. Mannheim, *Ber.*, 50, 708, 1917; R. Strebinger, *Chem. Ztg.*, 42, 242, 1918; F. G. Germuth, *Chemist-Analyst*, 17, 3, 7, 1928; *ib.*, 19, 4, 1930. Strebinger (l.c.) says that when the nickel exceeds 25 mgrms. some of the precipitant is occluded, leading to high results. In such cases he recommends ignition to nickel oxide. Other dioximes have been used for the detection and determination of nickel, *e.g.* oxalenediuramido-oxime (F. Feigl and A. Christiani-Kronwald, *Zeit. anal. Chem.*, 65, 341, 1925); α-furildioxime (B. A. Soule, *Journ. Amer. Chem. Soc.*, 47, 981, 1925; H. F. Harwood and L. S. Theobald, *Analyst*, 58, 673, 1933).

acetates, tartrates, citrates, etc.[1] In Fresenius and Bergmann's process,[2] which is most generally used, the double sulphate of ammonium and nickel, or ammonium and cobalt, in ammoniacal solution, is employed. The presence of sodium phosphate [3] or ammonium sulphate is favourable to the deposition of these metals. Cobalt deposits rather more slowly than nickel, and the results with cobalt are usually a little too high.

The Electrolyte.—Mix the given solution with 5–10 grms. of ammonium sulphate and 30–40 c.c. of concentrated ammonia for every 0·25–0·30 grm. of the nickel or cobalt sulphate or chloride [4] in the solution under investigation. Dilute the solution with distilled water until it occupies a volume of about 150 c.c.

The Electrolysis.—The solution is electrolysed at the room temperature [5] with a current density of 1·0 to 1·5 amps., and 2·8 to 3·5 volts. The electrolysis is completed in the case of nickel in about $2\frac{1}{2}$ to 3 hours; and in the case of

[1] W. Gibbs, *Zeit. anal. Chem.*, 3, 336, 1864; 11, 10, 1872; 22, 558, 1883; F. Wrightson, *ib.*, 15, 300, 1876; T. Schweder, *ib.*, 16, 344, 1877; W. Ohl, *ib.*, 18, 523, 1879; C. Luckow, *Dingler's Journ.*, 177, 235, 1850; J. M. Merrick, *Chem. News*, 24, 100, 1871; A. Riche, *Compt. rend.*, 85, 226, 1877; *Ann. Chim. Phys.*, (5), 13, 508, 1878; A. Classen and M. A. von Reis, *Ber.*, 14, 1622, 1881; L. Schucht, *Zeit. anal. Chem.*, 22, 485, 1883; *Chem. News*, 47, 209, 1883; F. Oettel, *Zeit. anal. Chem.*, 27, 15, 1888; C. A. Kohn and J. Woodgate, *Journ. Soc. Chem. Ind.*, 8, 256, 1889; A. Brand, *Zeit. anal. Chem.*, 28, 581, 1889; G. A. Le Roy, *Compt. rend.*, 112, 722, 1891; F. Rüdorff, *Zeit. angew. Chem.*, 5, 3, 197, 1892; C. Winkler, *Zeit. anorg. Chem.*, 4, 10, 1893; *ib.*, 8, 1, 1895; C. Vortmann, *Monats.*, 14, 536, 1894; *Chem. Centr.*, (1), 877, 1894; E. D. Campbell and W. H. Andrews, *Journ. Amer. Chem. Soc.*, 17, 125, 1895; A. Hollard, *Compt. rend.*, 123, 1063, 1896; O. Ducru, *ib.*, 125, 436, 1897; L. Wolman, *Elektrochem. Zeit.*, 3, 537, 1897; D. Balachowsky, *Compt. rend.*, 132, 1492, 1901; A. Hollard, *Bull. Soc. chim.*, (3), 29, 116, 1903; F. Exner, *Journ. Amer. Chem. Soc.*, 25, 899, 1903; A. Hollard and L. Bertiaux, *Compt. rend.*, 137, 853, 1903; *ib.*, 138, 1605, 1904; *Bull. Soc. chim.*, (3), 31, 900, 1904; A. Fischer and R. J. Boddaert, *Elektrochem. Zeit.*, 10, 945, 1904; E. F. Smith, *Journ. Amer. Chem. Soc.*, 26, 1595, 1904; L. G. Kollock and E. F. Smith, *ib.*, 27, 1255, 1527, 1905; *ib.*, 29, 797, 1907; F. M. Perkin and W. C. Prebble, *Trans. Faraday Soc.*, 1, 103, 1905; J. E. Root, *Journ. Phys. Chem.*, 9, 1, 1905; A. Thiel and A. Windelschmidt, *Elektrochem. Zeit.*, 12, 737, 1906; F. Foerster, *ib.*, 13, 563, 1907; F. Foerster and W. Treadwell, junr., *ib.*, 14, 89, 1908; A. Fischer, *Chem. Ztg.*, 32, 185, 1908; A. Thiel, *Elektrochem. Zeit.*, 14, 201, 1908; A. Schumann, *Zeit. angew. Chem.*, 21, 2579, 1908; G. Lambris, *Elektrochem. Zeit.*, 15, 973, 1909; C. S. Tatlock, *Zeit. anal. Chem.*, 48, 433, 1909; J. T. Stoddard, *Journ. Amer. Chem. Soc.*, 31, 385, 1909; E. P. Alvarez, *Ann. Chim. anal.*, 14, 169, 1910; P. Bruylants, *Bull. Soc. chim. Belg.*, 23, 383, 1909; *ib.*, 24, 367, 1910; R. C. Benner and W. H. Ross, *Journ. Amer. Chem. Soc.*, 33, 493, 1911; L. Bertiaux, *Ann. Chim. anal.*, 18, 377, 1913; E. P. Later, *Foundry*, 41, 243, 1913; H. König, *Chem. Ztg.*, 37, 1106, 1913; W. J. Marsh, *Journ. Phys. Chem.*, 18, 705, 1914; T. L. Walker, *Trans. Roy. Soc. Canada*, (3), 9, 93, 1915; E. F. Smith, *Trans. Amer. Electrochem. Soc.*, 27, 3, 1915; J. Guzmán and E. Jimeno, *Anal. Fis. Quim.*, 14, 250, 1916; S. Rothschild, *Chem. Ztg.*, 41, 29, 1917; P. Nicolardot and G. Gourman, *Bull. Soc. chim.*, (4), 25, 338, 1919; M. Matsui and T. Nakazawa, *Journ. Tokyo Chem. Soc.*, 40, 339, 1919; *Mem. Coll. Sci. Kyoto*, 4, 265, 1920; E. Fernandez-Espina, *Anal. Fis. Quim.*, 17, 199, 1919; N. H. Furman, *Journ. Amer. Chem. Soc.*, 42, 1789, 1920; G. E. F. Lundell and J. I. Hoffman, *Journ. Ind. Eng. Chem.*, 13, 540, 1921; K. Wagenmann, *Metall und Erz.*, 18, 447, 1921; E. Rousseau, *Chim. et Ind.*, 13, 199, 1925; C. Marie and J. Berthelot, *Compt. rend.*, 183, 793, 1926; W. Moldenhauer, *Zeit. angew. Chem.*, 39, 640, 1926; B. Tougarinov, *Bull. Soc. chim. Belg.*, 39, 331, 1930; D. H. Brophy, *Ind. Eng. Chem. Anal. Ed.*, 3, 363, 1931; H. Danneel and H. Nissenson, *Inter. Cong. angew. Chem.*, 4, 679, 1903; G. Ferreri, *Giorn. Chim. Ind. appl.*, 5, 339, 1923; J. Hope, *Journ. Soc. Chem. Ind.*, 9, 375, 1890; E. P. Smith, *Electro-Analysis*, Philadelphia, 275, 1918. For errors in the electrolysis of alkaline solutions, see E. Reichel, *Zeit. anal. Chem.*, 89, 411, 1932.

[2] H. Fresenius and F. Bergmann, *Zeit. anal. Chem.*, 19, 314, 1880.

[3] M. S. Cheney and E. S. Richards, *Amer. J. Science*, (3), 14, 178, 1877.

[4] Nitrates should be absent. If nitrates be present in the solution, evaporate to dryness with sulphuric acid in order to expel the nitric acid. According to W. J. Marsh (*l.c.*), both nitrates and chlorides must be absent, while A. Schumann (*l.c.*) says that neither nitrates nor chlorides interfere. A. Thiel (*l.c.*) concludes that nitrates are innocuous, provided no trace of nitrite is present.

[5] If the solution is electrolysed at, say, 45°–50°, $1\frac{1}{4}$ to 2 hours are needed for the electrolysis.

cobalt, in 5 to 6 hours.[1] Break the current; pour off the exhausted electrolyte (page 257); wash, dry and weigh the deposit.

The deposited nickel adheres firmly to the cathode and it has a bright silver-grey colour, sometimes closely resembling the appearance of the platinum itself. The cobalt deposit is generally brown or black in colour. It is rare to see a brilliant cobalt deposit. The results with the dark-coloured cobalt deposits are quite as satisfactory as with a bright deposit.

If too little ammonia has been used in the electrolyte, some nickel may be deposited on the anode, giving low results. Too much ammonia retards the deposition of the metals. The presence of ammonium chloride or ammonium nitrate also retards the deposition of the metals.[2]

A couple of test experiments quoted from Fresenius and Bergmann's paper show that good results can be obtained. This agrees with general experience.

	Nickel.	Cobalt.
Used	0·1233	0·1280 grm.
Found	0·1233	0·1286 grm.

Treatment of Mixed Cobalt and Nickel Sulphides.—In actual analyses, mixed cobalt and nickel sulphides are often obtained. To prepare these for analysis, ignite the filter-paper in the usual way (page 416). Dissolve the sulphides and ash of the paper in hydrochloric acid with a little nitric acid. Evaporate the solution to dryness on a water bath. Dissolve the residue in a little dilute sulphuric acid and transfer the solution to the platinum basin for electrolysis; add 5 grms of ammonium sulphate, 40-60 c.c. of ammonia; dilute the solution to about 150 c.c. with distilled water; and proceed with the electrolysis as indicated above. Weigh the mixed deposit as metallic "cobalt + nickel." Dissolve the metals in hot nitric acid and determine either the nickel or the cobalt by one of the processes described in this work. The other metal can be obtained by difference.

Removal of the Deposit from the Electrode.—Nickel is difficult to remove from the cathode, because it is inclined to become "passive." Warm nitric or sulphuric acid may be used for dissolving the metal. Owing to the close resemblance between the deposited nickel and the platinum, special care must be taken to dissolve off all the nickel before the cathode is heated ready for the next determination. It is very difficult to remove the stain left on platinum when it has been heated in contact with nickel. The removal of cobalt presents no particular difficulty, since it does not assume the passive condition and it is readily soluble in concentrated nitric acid.

§ 208. The Determination of Cobalt as Phosphate—Dirvell's Process.

Cobalt can be determined conveniently as cobalt ammonium phosphate, $CoNH_4PO_4.H_2O$,[3] or as cobalt pyrophosphate, $Co_2P_2O_7$, though the method

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[1] To test for the end of the electrolysis in the colourless solution, transfer about 1 c.c. by means of a pipette to a test tube. Add H_2S water. A brown coloration will show that the metal is not all deposited. Yellow ammonium sulphide is not so good for making the test, because its yellow colour may mask the colour produced by small quantities of nickel or cobalt.

[2] If the electrolysis of ammoniacal solutions be too protracted, the cathode increases in weight as soon as all the nickel is deposited, possibly owing to the dissolution of the anode— F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, 2, 115, 1911.

[3] P. Dirvell, *Compt. rend.*, 89, 903, 1879; *Chem. News*, 40, 268, 1879; J. Clark, *ib.*, 48, 262, 1883; *Proc. Glasgow Phil. Soc.*, 15, 183, 1884; J. Hope, *Journ. Soc. Chem. Ind.*, 9, 375, 1890; H. D. Dakin, *Zeit. anal. Chem.*, 39, 784, 1900; C. S. Tatlock, *ib.*, 48, 433, 1909; L. Dufty, *Journ. Iron Steel Inst.*, 90, 52, 1914; W. R. Schoeller and A. R. Powell, *Analyst*, 41,

is somewhat inferior in accuracy to the electrolytic or α-nitroso-β-naphthol process.

Precipitation of Cobalt Ammonium Phosphate.—The solution, containing about 0·1 grm. of cobalt per 100 c.c., after adjustment to the faintest acidity, is heated almost to boiling. A solution of microcosmic salt, at the rate of 5 to 8 grms. of the salt in 20 c.c. of water for every 0·1 grm. of cobalt present, is then added drop by drop with constant stirring. The mixture is digested without boiling over a mushroom-headed burner or heated on a water bath, until the bulky violet precipitate changes into a compact red crystalline form. The precipitate is now filtered through a Gooch crucible, which has previously been dried for 1½ hours at 105° and weighed. The filtrate is used to transfer the last traces of the precipitate from the beaker to the crucible. Finally the precipitate is washed free from soluble phosphates with hot water. The crucible and contents are dried as previously for 1½ hours and the precipitate weighed as $CoNH_4PO_4.H_2O$ containing 39·44 per cent. of cobalt oxide, CoO.

A little cobalt escapes precipitation. This is recovered by making the filtrate ammoniacal and passing hydrogen sulphide through it. The precipitated cobalt sulphide is filtered off, washed, strongly ignited and weighed as Co_3O_4.

The cobalt ammonium phosphate can be ignited in the crucible to pyrophosphate and weighed as such, but care must be taken in the early stages of the ignition to guard against loss by spurting during the evolution of water and ammonia from the decomposing precipitate:—

$$2CoNH_4PO_4.H_2O = Co_2P_2O_7 + 2NH_3 + 3H_2O$$

If this procedure is adopted the crucible should be initially ignited and not merely dried at 105°.

The Influence of Nickel.—It is stated that, if the precipitation is made in faintly ammoniacal solution, any nickel present remains in solution so that the process can be used for separating cobalt from nickel, provided the amount of microcosmic salt is proportionately increased to allow for the nickel present. However, when nickel is present a double precipitation is advisable. It is clearly impossible in the presence of nickel to recover the cobalt in the filtrate by precipitation as sulphide, since the nickel will be simultaneously precipitated. A better method, particularly when only small amounts of nickel are present, as in cobalt oxides (see page 429), is first to separate the nickel by the glyoxime process. The excess of glyoxime in the filtrate is then destroyed by evaporating to small bulk with a slight excess of concentrated hydrochloric or nitric acid. The solution, after dilution and neutralisation, is now ready for the precipitation of the cobalt as phosphate.[1]

124, 1916; **42**, 189, 1917; **44**, 275, 1919; *Journ. Iron Steel Inst.*, **97**, 441, 1918; F. Ibbotson and L. Aitchison, *The Analysis of Non-Ferrous Alloys*, 158, 1922; H. H. Willard and D. Hall, *Journ. Amer. Chem. Soc.*, **44**, 2226, 1922; L. A. Congdon and T. H. Chen, *Chem. News*, **128**, 132, 1924.

[1] For the separation of cobalt from nickel as xanthate, see W. R. Schoeller and A. R. Powell, *Analyst*, **44**, 275, 1919; L. Compin, *Ann. Chim. anal.*, (2), **2**, 218, 1920; A. Whitby and J. P. Beard, *Journ. Chem. Met. Min. Soc. S. Africa*, **21**, 199, 1921. Thiophenylhydantoic acid has been recommended for the separation of cobalt from a number of elements, other than nickel—H. H. Willard and D. Hall, *Journ. Amer. Chem. Soc.*, **44**, 2219, 1922.

§ 209. The Colorimetric Determination of Small Quantities of Cobalt.

Lampadius' attempt [1] to determine small quantities of cobalt from the reddish-brown colour produced when ammonia is added to the solution of a cobalt salt was not very successful. The colour changes on exposure to the air.[2] Müller used a colorimeter for estimating the amount of cobalt. This measured the cobalt in terms of the intensity of the colour of solutions of its salts [3]; and Winkler, recognising that the colour of cobalt solutions is complementary to that of nickel solutions,[4] and that the one solution therefore neutralises the tint of the other, found that the maximum decolorisation occurred when the proportion of nickel to cobalt was as 3 : 1. Hence Winkler proposed adding nickel or cobalt to a given solution until the maximum decolorisation occurred. This furnished data sufficient to compute an approximation to the amount of nickel and of cobalt in a given solution. The process is not very reliable.

Skey,[5] as indicated on page 411, found that, when solutions of cobalt thiocyanate are shaken up with ether and amyl alcohol, a blue superincumbent layer is obtained, and this reaction is sometimes inaptly called "Vogel's test" for cobalt. Skey suggested shaking out the cobalt thiocyanate with ether as a means of separating cobalt and nickel; and this idea was later used by Rosenheim and Huldschinsky,[6] and recommended for separating cobalt and nickel by a process similar to that used by Rothe (page 505) for separation of iron.

The red colour of ferric thiocyanate, if present, masks the blue colour of the cobalt thiocyanate and, in consequence, the iron must be removed. Wolff [7] proposed removing the iron by first adding an excess of ammonium thiocyanate, and then sodium carbonate until the blood-red colour of the ferric thiocyanate disappeared. The precipitated ferric hydroxide was removed by filtration, and the filtrate shaken with ether to get the cobalt-blue coloration. This is quite satisfactory. Bettink preferred reducing the ferric iron to the ferrous condition by means of sodium thiosulphate until the red colour of the ferric thiocyanate disappeared. The filtered solution was then

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[1] W. A. Lampadius, *Journ. prakt. Chem.*, (1), **13**, 385, 1838.

[2] T. Bodemann, *Anleitung zur Berg- und Hüttenmännischen Probierkunst*, Clausthal, 456, 1857.

[3] A. Müller, *Das complementar Colorimeter*, Chemnitz, 1854; *Journ. prakt. Chem.*, (1), **60**, 474, 1853; F. Dehms, *Zeit. anal. Chem.*, **3**, 218, 494, 1864.

[4] R. Wagener, *Journ. prakt. Chem.*, (1), **61**, 129, 1854; C. Winkler, *ib.*, (1), **97**, 414, 1866; R. W. Challinor, *Journ. Roy. Soc. N.S.W.*, **38**, 406, 1905; E. J. Maumené, *Compt. rend.*, **30**, 209, 1850; J. H. Gladstone, *Phil. Mag.*, (4), **9**, 535, 1855; T. Bayley, *ib.*, (5), **6**, 15, 1878; *Journ. Chem. Soc.*, **37**, 828, 1880; J. Bottomley, *Proc. Manchester Lit. Phil. Soc.*, **19**, 164, 1880; *Chem. News*, **42**, 56, 1880; M. Knieder, *Berg. Hütt. Ztg.*, **53**, 243, 1894; F. Dehms, *Dingler's Journ.*, **172**, 440, 1864; **173**, 436, 1864.

[5] W. Skey, *Chem. News*, **16**, 201, 1867; H. W. Vogel, *Ber.*, **8**, 1533, 1875; **12**, 2314, 1879; *Zeit. anal. Chem.*, **21**, 563, 1882; T. T. Morrell, *ib.*, **16**, 251, 1877; *Pharm. Centr.*, **17**, 394, 1877; W. H. Bettink, *Nederl. Tijdschr. Pharm.*, **11**, 43, 1899. H. Ditz (*Chem. Ztg.*, **25**, 109, 1901) studied the changes of colour of cobalt salts by the action of glycerine, ether, alcohol, acetone, etc. Skey isolated blue acicular crystals from the ethereal solution of cobalt thiocyanate. F. P. Treadwell (*Zeit. anorg. Chem.*, **26**, 108, 1901) later represented the composition of the crystals by the formula $(NH_4)_2Co(SCN)_4$.

[6] A. Rosenheim and E. Huldschinsky, *Zeit. anal. Chem.*, **40**, 809, 1901; *Ber.*, **34**, 2050, 1901; A. Rosenheim and A. Cohn, *ib.*, **33**, 1111, 1900; F. W. Dootson, *Proc. Cambridge Phil. Soc.*, **12**, 125, 1903.

[7] C. H. Wolff, *Zeit. anal. Chem.*, **18**, 38, 1879; C. Zimmermann, *ib.*, **20**, 414, 1881; *Liebig's Ann.*, **199**, 1, 1879; W. H. Bettink, *Nederl. Tijdschr. Pharm.*, **11**, 64, 1899.

treated with ether as before. There are several objections to the use of sodium thiosulphate. These reactions can be applied to the colorimetric determination of small quantities of cobalt [1] in the following manner:—

Standard Solution.—Pipette 1 c.c. of a standard solution of cobalt sulphate [2] into a graduated Nessler's tube,[3] 25 to 30 c.c. capacity. Add 1 c.c. of dilute sulphuric acid; 5 c.c. of water; 0·2 grm. of solid ammonium thiocyanate; [4] and water up to the 10 c.c. mark.

Test Solution.—Add 1 grm. of ammonium thiocyanate per 50 c.c. of the solution under investigation,[5] and then add concentrated sodium carbonate—Na_2CO_3—until the red colour of the ferric thiocyanate disappears.[6] Filter and wash. Neutralise the filtrate with dilute sulphuric acid, and make the solution up to 100 c.c. Pipette, say, 5 c.c. into a Nessler's tube; add 1 c.c. of dilute sulphuric acid; and make the solution up to the 10 c.c. mark with water.

The Comparison.—Fill both tubes up to the 20 c.c. mark with a mixture of ether and amyl alcohol.[7] Shake the mixture. As soon as the ethereal and aqueous layers have separated compare the colours of the ethereal solutions, and note if more or less standard solution is needed to make the tints of the two solutions the same. Add a diluted solution (say 1 in 10 c.c.) of the standard cobalt solution to the paler-tinted solution from a burette reading to $\frac{1}{50}$ c.c., and an equivalent amount of water to the other solution, until the tints of the two solutions are the same. Or make up other standard solutions, if necessary, containing more or less standard cobalt sulphate, until the tints of the standard and test solutions are the same. The calculations are then made in the usual way.

EXAMPLE.—Suppose 5 c.c. of the "filter press water" of a pottery be evaporated to dryness and the residue washed, and its solution, about 5 c.c., be treated as described above. After a comparison the test solution was the paler. It required 2·58 c.c. of diluted cobalt sulphate (10 c.c. of standard was made up to 100 c.c. with water) to equalise the tints. Hence the standard solution had 0·00001 grm. of cobalt, and the test solution $x + 0.00000258$ grm. of cobalt. Hence $x = 0.00000742$ grm. of cobalt per 5 c.c. of filter press water. But this is equivalent to $0.00000742 \times 2.203 = 0.00001635$ grm. cobalt chloride, $CoCl_2$, per 5 c.c., or 0·00327 grm. per litre; or the equivalent of 0·00052 oz. of anhydrous cobalt chloride was escaping per gallon of the filter press water.

The aqueous layer retains about one-tenth of its volume of ether, and also a trace of cobalt; but since the standard and test solutions are similar, the error is negligibly small. Otherwise the ethereal solutions would have to be removed and the aqueous layer washed out with ether, and the two solutions compared in any convenient way.

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[1] J. W. Mellor, *Trans. Cer. Soc.*, 8, 132, 1909; A. D. Powell, *Journ. Soc. Chem. Ind.*, 36, 273, 1917; E. S. Tomula, *Suomen Kem.*, 2, 72, 1929; *Zeit. anal. Chem.*, 83, 6, 1931; W. Heinz, *ib.*, 78, 427, 1929.

[2] STANDARD SOLUTION OF COBALT SULPHATE.—Dissolve 0·01 grm. of cobalt in dilute sulphuric acid and make the solution up to a litre with water. Alternatively, take 0·0477 grm. of pure, nickel-free cobalt sulphate, $CoSO_4.7H_2O$. This gives a solution containing 0·01 grm. cobalt per 1000 c.c. or 1 c.c. is equivalent to 0·00001 grm. of cobalt.

[3] The Nessler's cylinders are about 17 cm. high and 13 mm. internal diameter, and made from colourless glass. The cylinders should be as nearly alike as possible, and stoppered. See page 75.

[4] All the reagents must be free from iron—see page 185.

[5] Say, a solution obtained during the analysis of a "stained body or glaze."

[6] If no iron is present, the treatment with sodium carbonate is unnecessary.

[7] ETHER-ALCOHOL MIXTURE.—Methylated ether, 5 vols.; isoamyl alcohol, 5 vols.

This method is useful for estimating the small amounts of "cobalt" used for "bleaching" china clays and pottery bodies.[1]

§ 210. The Evaluation of Cobalt and Nickel Oxides.

The standard for commercial "black oxide" of cobalt is 70 per cent. of metallic cobalt, corresponding with 89 per cent. of cobalt monoxide—CoO; but it generally contains the equivalent of 71 to 72 per cent. metallic cobalt. The standard for "prepared oxide" is 74·5 per cent. of metal, corresponding with 94·7 per cent. of CoO; but commercial samples sometimes run as high as 76 to 77 per cent. of metallic cobalt. This corresponds with 96·6 to 98 per cent. of cobalt oxide—CoO. Hence, in evaluating these oxides, a determination of the percentage of cobalt or nickel as metal generally suffices.[2] A qualitative test should always be made. If any of the metals indicated below be absent, the process can be abbreviated accordingly.

Assume, in the extreme case, that the oxide contains silica, some metals in the hydrogen sulphide group, iron, aluminium, manganese, zinc, nickel and cobalt. In evaluating the oxide, therefore, everything is got into solution and the impurities are removed, step by step. For a full analysis, the method indicated in the schemes, pages 327 and 413, may be used; for the cobalt and nickel oxides alone, proceed as described below.

1. *Dissolution of the Oxide.*—Digest half a gram of the oxide in a 200 c.c. beaker with 10 c.c. of concentrated hydrochloric acid. Filter, wash and ignite the residue. Fuse the residue with sodium carbonate; take up the mass with hydrochloric acid; evaporate the mixed solutions to dryness in a basin.

2. *Removal of Silica, Iron and Aluminium.*—Add 35 c.c. of concentrated ammonia and a few grams of solid ammonium chloride, and warm the mixture until the residue is disintegrated; filter; wash with hot water and keep the filtrate. Poke a hole in the tip of the filter-paper and rinse the residue on the filter-paper back into the basin; pour hot dilute hydrochloric acid (1 : 2) through the filter-paper to dissolve any traces of the residue, collecting the runnings in the basin under the funnel; wash; boil until solution is complete; add ammonium chloride and excess of ammonia to the boiling solution; filter; wash thoroughly with hot water; and unite the two filtrates.[3]

3. *Precipitation of Copper by Hydrogen Sulphide.*—Boil off any excess of ammonia; just acidify the solution with hydrochloric acid; and then add 5 c.c. of the concentrated acid in excess; boil a few minutes; dilute to about 250 c.c. with water; pass hydrogen sulphide through the hot solution (70°–80°) to precipitate copper, lead, etc. Filter and wash with water saturated with hydrogen sulphide; boil the filtrate to expel the hydrogen sulphide.

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[1] For alternative methods, see C. Hüttner, *Zeit. anorg. Chem.*, 86, 341, 1914; F. W. Atack, *Journ. Soc. Chem. Ind.*, 34, 641, 1915; E. G. Jones, *Analyst*, 43, 317, 1918; C. Brenner, *Helv. Chim. Acta*, 3, 90, 1920; S. A. Braley and F. B. Hobart, *Journ. Amer. Chem. Soc.*, 43, 482, 1921; A. Blanchetière and J. M. Pirlot, *Compt. rend. Soc. biol.*, 101, 858, 1929; M. Delaville, *ib.*, 101, 1082, 1929. See W. Heinz (*Zeit. anal. Chem.*, 78, 427, 1929) for the accuracy and available range of various methods. For the colorimetric determination of nickel by the use of potassium thiocarbonate, see M. Lucas, *Bull. Soc. chim.*, (3), 21, 432, 1899; *Chem. News*, 80, 39, 1899; V. Lindt, *Zeit. anal. Chem.*, 53, 165, 1914. See also L. T. Fairhall, *Journ. Ind. Hygiene*, 8, 528, 1926; A. P. Rollet, *Compt. rend.*, 183, 212, 1926; B. Jones, *Analyst*, 54, 582, 1929; G. Denigès, *Bull. Soc. pharm. Bordeaux*, 70, 106, 1932.

[2] For the analysis of cobalt ores, see H. Copaux, *Bull. Soc. chim.*, (3), 29, 301, 1903; and for the analysis of nickel ores, A. Hollard, *Ann. Chim. anal.*, 8, 401, 1903.

[3] The amount of iron and alumina is usually too small for the result to be affected by the adsorption of salts of nickel and cobalt by the precipitated iron; if otherwise, use the basic acetate separation.

4. *Removal of Manganese.*—Add a slight excess of ammonia; acidify the solution strongly with acetic acid; add 1 to 2 grms. of ammonium acetate; heat the solution to 70° or 80°; saturate the solution with hydrogen sulphide; filter and wash with hot water. The manganese remains in solution; the cobalt, zinc and nickel are precipitated. The filtrate probably still contains traces of cobalt and nickel. To precipitate these, concentrate the solution by evaporation; add colourless ammonium sulphide; acidify the solution with acetic acid; warm, and filter, if necessary, into a separate beaker. Test the filtrate in the same way and, if necessary, repeat the operation.

5. *Removal of Zinc.*—Wash the precipitated sulphides from the paper as completely as possible; dry and burn the paper; dissolve everything in hydrochloric acid with a little nitric acid. The solution contains cobalt, nickel and zinc. To remove the latter, add 2 or 3 grms. of finely crystalline ammonium chloride [1]; evaporate the solution to dryness on a water bath; heat the solid mass until all the ammonium chloride is expelled. Zinc is volatilised at the same time. When cold, dissolve the mass in aqua regia and evaporate to dryness. The solution is now ready for the separation of cobalt and nickel as described on pages 415 *et seq.* The zinc can also be removed by precipitation as sulphide in the presence of formic acid (see page 385).

Smalt or zaffre may be fused with sodium carbonate and sodium nitrite (page 510), or broken down by treatment with acids. The silica can be separated by evaporation of the hydrochloric acid solution (page 147), and the filtrate treated as described above for the separation of iron or by the basic acetate process (page 383). Nickel, cobalt, bismuth, iron, lead and arsenic, as well as silica, alumina, alkalies and alkaline earths, may be present. The matt blues rich in alumina are best fused with potassium bisulphate, or pyrosulphate. Zinc, phosphoric and arsenic oxides, as well as cobalt, nickel and silica, may here be present.

§ 211. The Volumetric Determination of Cobalt and Nickel.

The methods which have been suggested up to the present for the determination of cobalt volumetrically are not satisfactory except under special conditions, and hence no volumetric method for cobalt [2] has won a place in general practice.

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[1] R. Fresenius (*Zeit. anal. Chem.*, **21**, 229, 1882) says that 5 grms. of ammonium chloride suffice for 0·2 grm. of zinc oxide.

[2] C. Winkler (*Zeit. anal. Chem.*, **3**, 420, 1864) titrates with potassium permanganate in the presence of mercuric oxide. H. B. Harris (*Journ. Amer. Chem. Soc.*, **20**, 173, 1898) obtained fair results with hot dilute solutions, not with concentrated solutions. N. McCulloch (*Chem. News*, **59**, 51, 1889) oxidises cobalt cyanide with potassium dichromate and titrates the excess of dichromate with Mohr's salt. E. Fleischer (*Journ. prakt. Chem.*, (2), **110**, 48, 1870) precipitates the cobalt with alkali hypochlorite, adds an excess of Mohr's salt, and titrates back with potassium permanganate. E. Donath (*Ber.*, **12**, 1868, 1879; *Chem. News*, **41**, 15, 1880) oxidises the cobalt by means of iodine in an alkaline solution, and distils the Co_2O_3 with hydrochloric acid into a solution of potassium iodide, and titrates the liberated iodine with thiosulphate. M. A. von Reis and F. Wiggart (*Zeit. angew. Chem.*, **3**, 695, 1890) boil the cobaltous salt with zinc emulsion, add an excess of potassium permanganate, and titrate back with a solution of Mohr's salt. C. Rössler, *Liebig's Ann.*, **200**, 323, 1880; E. Rupp and F. Pfennig, *Chem. Ztg.*, **34**, 322, 1910; G. S. Jamieson, *Journ. Amer. Chem. Soc.*, **32**, 757, 1910; A. Metzl, *Zeit. anal. Chem.*, **53**, 537, 1914; W. R. Schoeller and A. R. Powell, *Analyst*, **41**, 124, 1916; W. D. Engle and R. G. Gustavson, *Journ. Ind. Eng. Chem.*, **8**, 901, 1916; E. Müller and H. Lauterbach, *Zeit. anal. Chem.*, **62**, 23, 1923; E. Müller and W. Schluttig, *Zeit. anorg. Chem.*, **134**, 327, 1924; A. A. Vassiliev, *Zeit. anal. Chem.*, **78**, 439, 1929; S. Glasstone and J. C. Speakman, *Analyst*, **55**, 93, 1930; B. S. Evans, *ib.*, **62**, 363, 1937. H. H. Willard and D. Hall (*Journ. Amer. Chem. Soc.*, **44**, 2237, 1922) consider that, in general, volumetric methods are the most accurate and satisfactory for the determination of cobalt.

Volumetric methods for nickel also fail in the presence of cobalt, although the cyanide process for nickel [1] is quite good when cobalt is absent, or only present in minute quantities, and when copper, silver, gold and metals of the platinum group are absent.

Theory of the Cyanide Process.—The cyanide process, suggested by Moore and by Campbell and Andrews, depends on the fact that, if potassium cyanide be added to a feebly ammoniacal solution of a nickel salt, a double cyanide is formed—

$$NiCl_2 + 4KCN = 2KCl + Ni(CN)_2 . 2KCN$$

and if the solution contains a little silver iodide (or a mixture of silver nitrate and potassium iodide) the solution will remain turbid until enough potassium cyanide has been added to transform all the nickel to the double cyanide. Further additions of potassium cyanide dissolve the silver iodide to a clear solution. Thus —

$$AgI + 2KCN = AgCN.KCN + KI$$

When the silver iodide is all dissolved, it will be obvious that the transformation of the nickel to the double cyanide is completed. Hence the potassium cyanide used in the titration represents the amount of potassium cyanide used for the formation of the double cyanide, and for the dissolution of the silver iodide. If the amount of the potassium cyanide needed for the dissolution of the silver iodide be known, the amount needed for the transformation of the nickel can be found by subtraction.

The Determination.—Add 2 c.c. of concentrated sulphuric acid to the solution under investigation. Neutralise the solution with ammonia.[2] Add 20 c.c. of 2N-NH_3 to the neutral solution, and then 2 c.c. of a 2 per cent. solution of potassium iodide, and 5 c.c. of a solution of silver nitrate (5·79 grms. per litre).[3] The solution will now be turbid owing to the presence of silver iodide. Titrate [4] the cold solution with a standard solution of potassium cyanide [5] until

[1] T. Moore, *Chem. News*, **59**, 160, 292, 1889; **72**, 92, 1895; H. Brearley and H. Jervis, *ib.*, **78**, 177, 196, 1898; E. D. Campbell and W. H. Andrews, *Journ. Amer. Chem. Soc.*, **17**, 125, 1895; E. D. Campbell and W. Arthur, *ib.*, **30**, 1116, 1908; *Chem. News*, **98**, 38, 1908; G. W. Sargent, *Journ. Amer. Chem. Soc.*, **21**, 854, 1899; C. M. Johnson, *ib.*, **29**, 1201, 1907; H. Grossmann, *Chem. Ztg.*, **32**, 1223, 1908; H. Grossmann and B. Schück, *Zeit. anal. Chem.*, **47**, 169, 1908; G. Raulin, *Monit. Scient.*, **74**, 84, 1911; E. P. Later, *Foundry*, **41**, 243, 1913; E. F. Kern and M. H. Morris, *School Mines Quart.*, **35**, 1, 1914; G. L. Kelley and J. B. Connant, *Journ. Ind. Eng. Chem.*, **8**, 804, 1916; G. H. Stanley, *Journ. S. African Assoc. Anal. Chem.*, **4**, 10, 1921; A. and H. Eder, *Chem. Ztg.*, **46**, 1085, 1922; E. Müller and H. Lauterbach, *Zeit. anal. Chem.*, **61**, 457, 1922; E. Müller and W. Schluttig, *Zeit. anorg. Chem.*, **134**, 327, 1924; L. A. Congdon and C. H. Belge, *Chem. News*, **128**, 67, 1924; T. Heczko, *Zeit. anal. Chem.*, **78**, 325, 1929; S. Glasstone and J. C. Speakman, *Analyst*, **55**, 93, 1930; E. Rupp and F. Pfennig, *Chem. Ztg.*, **34**, 322, 1910; W. R. Schoeller and A. R. Powell, *Journ. Iron Steel Inst.*, **97**, 441, 1918; R. D. Midson, *Chem. Eng. Min. Rev.*, **29**, 196, 1937.

[2] The ammonium sulphate so formed makes the indicator more sensitive. If barium, or elements which form insoluble sulphates, be present, use nitrates or chlorides, not sulphates.

[3] Since 1 grm. of silver nitrate corresponds with 0·766 grm. of potassium cyanide, 1 c.c. of the silver nitrate, containing the equivalent of 0·008 grm. of silver iodide, will require 0·00444 grm. of potassium cyanide, or 0·344 c.c. of the solution of potassium cyanide described below. The silver nitrate should be standardised by a blank experiment without nickel. Find how many cubic centimetres of the standard solution of potassium cyanide are required to dissolve the silver iodide corresponding with 1 c.c. of silver nitrate solution. Do not trust to the calculation.

[4] In some cases, *e.g.* in the presence of manganese, if the titration be left partly completed, a precipitate may separate. This interferes with the result later on. Hence the titration should be completed without delay. The ammonium sulphate retards the formation of the precipitate.

[5] STANDARD POTASSIUM CYANIDE.—Make 12·9 grms. of potassium cyanide and 5 grms. of potassium hydroxide up to a litre. The potassium hydroxide makes the solution more

the solution is clear, showing that the silver iodide is dissolved. A black background is best for the titration. Add more silver nitrate solution, say 3 c.c., so that the turbidity again reappears. Again titrate with the potassium cyanide drop by drop until the last drop clears up the opalescence. The temperature of the solution should not exceed 20°, or disturbing side reactions may set in.

EXAMPLE.—Suppose it be found that 31 c.c. of the potassium cyanide solution are needed for the whole titration, and that 1 c.c. of the potassium cyanide solution represents 0·0037 grm. NiO. Suppose 3 c.c. of silver nitrate are added to reproduce the turbidity the second time, and that 1 c.c. of the silver nitrate solution represents $\frac{1}{8}$ c.c. of the potassium cyanide solution. In all, $5 + 3 = 8$ c.c. of silver nitrate has been added, and this corresponds with $\frac{1}{8} \times 8 = 2\cdot7$ c.c. of the potassium cyanide. Hence the nickel corresponds with 31 less $2\cdot7 = 28\cdot3$ c.c. of potassium cyanide, or $28\cdot3 \times 0\cdot0037$, i.e. 0·105 grm. of NiO in the given solution.

Influence of Foreign Substances.[1]—Free alkalies, alkaline earths, alkali carbonates, chlorides, bromides, phosphates, have no marked effect. If not present in excessive amounts, chromates, manganese, arsenic, bismuth, molybdenum, tin, lead and uranium likewise have no marked effect. With manganese the indication is not quite so sharp or delicate. The manganese may be prevented from precipitating during the titration by the addition of ammonium chloride. For lead, use ammonium nitrate instead of sulphate, as indicated on page 347. If arsenic and antimony be present, use a little tartaric acid. Arsenic and tin should be oxidised with a little nitric acid and bromine water, and the excess boiled off.

The results with iron, aluminium, chromium and zinc are low. This is due to the precipitate[2] carrying down some nickel. If, therefore, these elements can be kept in solution, the titration is satisfactory. The chromium should be oxidised to chromate. Moore and Gel'band[3] recommend the use of sodium pyrophosphate for keeping the zinc, iron and aluminium in solution; while Brearley and Ibbotson recommend tartaric or citric acid to minimise the chances of error. Brearley and Ibbotson accordingly adopt the following procedure when iron and manganese have not been separated:—Add 3 grms. of citric acid and 2 grms. of ammonium sulphate per gram of sample. Add enough ammonia to make the solution feebly but distinctly alkaline. Add 2 c.c. of a 2 per cent. solution of potassium iodide, and silver nitrate until the turbidity is apparent. Titrate with potassium cyanide until the turbidity disappears. The alkaline citrate solution, containing iron in solution, is dark-coloured, and the changes are not easy to distinguish. Hence a strong beam of light should be sent across the solution. Fig. 99 shows Lupp's arrangement, useful for titrations which require strong illumination to distinguish the end point. The light is focussed in the body of the liquid from a reflecting mirror.[4]

If chromium be present, the turbidity disappears before the formation of

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stable. The cyanide can be standardised by dissolving 0·08 grm. of nickel in sulphuric acid, or 0·5384 grm. of nickel ammonium sulphate in water, and proceeding with the solution as described above. The cyanide should be freed from sulphur. This is sometimes effected by agitating the solution with lead monoxide or bismuth oxide.

[1] H. Brearley and F. Ibbotson, *The Analysis of Steel Works Materials*, London, 139, 183, 1902; C. M. Johnson, *Journ. Amer. Chem. Soc.*, 29, 1201, 1907.

[2] H. Brearley, *Chem. News*, 74, 16, 1896; G. T. Dougherty, *Iron Age*, 79, 1274, 1907.

[3] T. Moore, *Chem. News*, 59, 292, 1889; 72, 92, 1895; I. Gel'band, *Zavodskaya Lab.*, 3, 129, 1934.

[4] A. Lupp, *Zeit. anal. Chem.*, 34, 182, 1895. Compare W. C. Tobie, *Ind. Eng. Chem. News Ed.*, 15, 548, 1937; D. B. Pall, *Canadian Journ. Research*, 14B, 299, 1936.

the double nickel potassium cyanide is completed, but it soon returns. The phenomena of appearance and disappearance of the turbidity recur a number of times, and it is difficult to decide just when the reaction is at an end. Hence Johnson [1] prefers to use 12 grms. of citric acid instead of 3 grms. Johnson's plan then enables him to say that the titration can be accomplished "at almost the full speed of the burette."

If zinc be present, proceed as for iron and aluminium, but make the solution alkaline with sodium carbonate instead of ammonia. Copper should be removed by the thiocyanate process (page 365); then acidify the solution with nitric acid and proceed as described above. If the amount of the other interfering elements, e.g. cobalt, silver, gold, be known, an allowance can be made; otherwise, the result of the titration gives nickel plus cobalt, silver, gold and platinum, if these be present. Cobalt darkens the solution, owing to the oxidation of the cobaltocyanide to cobalticyanide. If the amount of cobalt be less than 10 per cent.
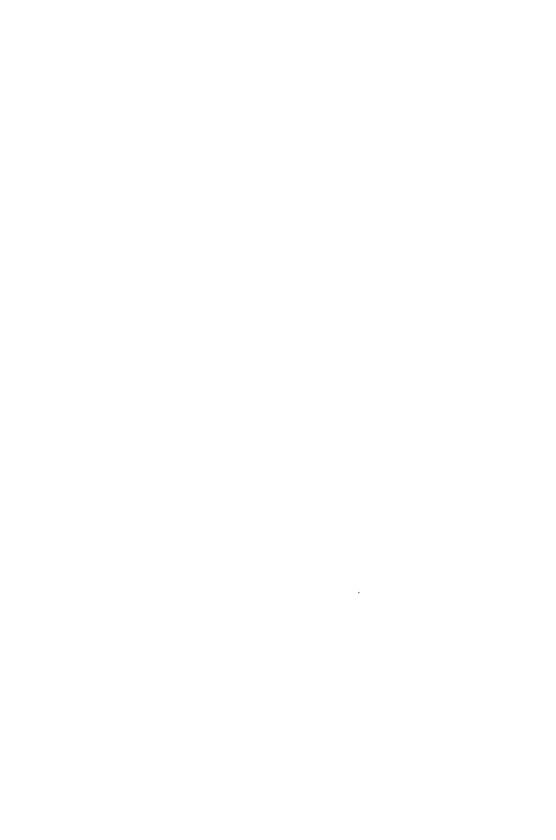
FIG. 99.—Illumination of Turbid Solutions during Titration.

of the total nickel, the sum Ni + Co can be determined by the titration, and the cobalt determined separately. Or the nickel can be precipitated with dicyano-diamide or dimethylglyoxime, dissolved in warm dilute hydrochloric acid and the ammoniacal solution titrated as described above.[2]

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[1] C. M. Johnson, *Rapid Methods for the Chemical Analysis of Special Steels*, New York, 105, 1909.

[2] For alternative volumetric methods, see R. Meurice, *Ann. Chim. anal.*, 18, 342, 1913; G. Zuccari, *Ann. Chim. appl.*, 3, 277, 1915; J. Holluta, *Monats.*, 40, 281, 1919; G. Spacu and R. Ripan, *Bul. Soc. Stiinte Cluj.*, 1, 325, 1922; P. Fluch, *Zeit. anal. Chem.*, 69, 232, 1926; L. A. Sarver, *Ind. Eng. Chem. Anal. Ed.*, 5, 275, 1933; J. T. Dobbins and J. P. Sanders, *ib.*, 6, 459, 1934; N. S. Krupenio, *Zavodskaya Lab.*, 6, 239, 1937.

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PART IV.

SPECIAL METHODS—BASES.

CHAPTER XXX.

THE DETERMINATION OF MOLYBDENUM, TUNGSTEN, COLUMBIUM AND TANTALUM.

§ 212. Molybdenum, Tungsten, Columbium and Tantalum in Silicate Analyses.[1]

THE "opening up" of minerals containing tungsten, molybdenum, columbium and tantalum [2] follows the lines indicated in different parts of this work (pages 139 and 264). First acids—single or mixed [3]—are tried. If these be impotent, fluxes—sodium peroxide,[4] potassium bisulphate or pyrosulphate [5]—are tried. Potassium hydroxide (or carbonate) is recommended as a general flux for the minerals containing the elements discussed in this chapter. The reason will appear later.

The oxides of these elements form soluble salts when fused with an excess of potassium carbonate or hydroxide. When the aqueous solution is treated with a slight excess of hydrochloric acid, a certain amount of the oxides separates and, if more acid be present, the soluble salts are decomposed and the separation of the oxide is often practically complete. Tungsten should be separated before proceeding to the ammonia and ammonium sulphide groups.[6]

In silicate analyses, therefore, the oxides of these elements may be found with the silica when the acid solution is evaporated to dryness.[7] If tungsten be the only member of this series present, the problem resolves into the separation of silica from tungsten oxide. Some molybdenum, if present, will separate with the silica as silicomolybdate. Columbium, tantalum, antimony,[8] tin,[9] arsenic [10] and phosphorus,[11] if present, may also be associated with the silica. Columbium, by the way, is often called niobium and symbolised Nb.

In dealing with complex mixtures of this type, it is generally best to extract the sodium or potassium carbonate fusion with water. The aqueous solution may contain one or more of the following: alkali tungstate, molybdate,

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[1] For the methods available for the determination of molybdenum, see J. P. Bonardi, *U.S. Bur. Mines Bull.*, **212**, iii, 71, 1923; for tungsten, C. W. Davis, *ib.*, **212**, iv, 131, 1923. A. C. Rice and L. A. Yerkes, *U.S. Bur. Mines Rep. Invest.*, **3328**, 37, 1937.

[2] For tantalum in clays, see A. Terreil, *Compt. rend.*, **51**, 94, 1860.

[3] For hydrochloric acid and aqua regia, see H. Bartonec, *Oestr. Chem. Ztg.*, **12**, 114, 1909. H. W. Hutchin and F. J. Fouks (*Trans. Inst. Min. Met.*, **18**, 425, 1909) recommend boiling alkali hydroxide (25 per cent. solution).

[4] *E.g.* W. Hempel (*Zeit. anorg. Chem.*, **3**, 193, 1895) decomposed wolframite in a few minutes by heating with four times its weight of sodium peroxide.

[5] *E.g.* H. Cremer, *Eng. Min. Journ.*, **59**, 345, 1895.

[6] W. F. Faggart and E. F. Smith (*Journ. Amer. Chem. Soc.*, **18**, 1051, 1896) show that if manganese sulphide be precipitated by ammonium sulphide in the presence of tungstic acid, some of the latter will contaminate the former.

[7] Molybdic oxide is soluble in an excess of acid.   [8] Antimony oxychloride.

[9] Stannous chloride gives a yellow precipitate with alkali tungstates and stannic tungstate is white.

[10] Tin or tungsten arsenate.   [11] Tin or tungsten phosphate; and phosphomolybdates.

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stannate, sulphate, aluminate, chloride, fluoride, arsenate, phosphate, antimonate, chromate, vanadate, columbate, tantalate and silicate, provided certain combinations which form insoluble precipitates are absent. The residue may contain alkali zirconate, ferric oxide, calcium, barium and strontium carbonates. The treatment for the separation of the different combinations revealed by a qualitative analysis may be based on the processes indicated in this work.

§ 213. The Detection of Tungsten, Tantalum, Molybdenum and Columbium.

Fuse, say, half a gram [1] of the finely powdered mineral with six times its weight of potassium hydroxide in a silver or nickel crucible. Extract the cold mass with hot water. Treat the filtered solution with 25 c.c. of hydrochloric acid (sp. gr. 1·16). Boil the solution and filter. The residue may contain columbium, tantalum, tin, tungsten, silica, molybdenum and antimony. Digest the moist residue with yellow ammonium sulphide. Molybdenum, tin, tungsten and antimony dissolve; silica, columbium and tantalum remain.

The ammoniacal sulphide solution containing molybdenum, tin, tungsten and antimony is acidified with hydrochloric acid and boiled; digest the washed precipitate with a little hydrochloric acid and a little nitric acid; filter and wash. The residue contains sulphur and tungsten, if present. Treat the solution with a few pieces of metallic zinc. Antimony and tin [2] are precipitated, molybdenum and zinc remain in solution. If the solution is blue, molybdenum is probably present.

Molybdenum.— Evaporate the solution along with a little nitric acid to dryness. Dissolve the residue in ammonia. (1) Pour a portion of the solution into moderately concentrated hydrochloric acid, add a few drops of a solution of potassium thiocyanate; if no red colour develops, iron is absent. Place a little metallic zinc in the acid solution; the development of a carmine-red colour indicates the presence of molybdenum. [3] (2) Another portion of the solution is heated with a few drops of sulphuric acid on the lid of a platinum crucible until it begins to fume. When cold, an ultramarine blue colour will develop when the acid is brought in contact with a little alcohol, if molybdenum be present. [4]

(3) *Permolybdate test.*—Evaporate the solution to be tested to dryness on a

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[1] More than this is sometimes required, say, 5 grms., but only if small quantities of these elements are present—P. Nicolardot, *Compt. rend.*, 144, 859, 1907.

[2] Note, if arsenic and antimony be present, poisonous hydrides may be evolved. For the recognition of tin and antimony, see any of the text-books on qualitative analysis.

[3] C. D. Braun, *Zeit. anal. Chem.*, 2, 36, 1863; P. E. Browning, *Amer. Journ. Sci.*, (4), 40, 349, 1915; J. Moir, *Journ. Chem. Met. Min. Soc. S. Africa*, 16, 191, 1916; G. A. Barbieri, *Atti R. Accad. Lincei*, (5), 28, (i), 351, 390, 1919; N. A. Tananaev and G. A. Pantschenko, *Ukraine Chem. Journ.*, 4, 121, 1929. The blood-red tint with ferric salts is destroyed by the addition of phosphoric acid. This is not the case with molybdenum—R. Fresenius, *Qualitative Chemical Analysis*, London, 185, 1897; F. C. Krauskopf and C. E. Swartz, *Journ. Amer. Chem. Soc.*, 48, 3021, 1926. The colour is feeble if the zinc and acid act for too long a time. E. Kedesdy (*Mitt. königl. Materialprüf.*, 31, 173, 1913) adds the thiocyanate after the reduction and extracts with ether, distilled over stannous chloride to remove peroxides. For the potassium iodide-mercurous nitrate test for molybdenum, see E. Kafka, *Zeit. anal. Chem.*, 51, 482, 1912; M. E. Pozzi-Escot, *Bull. Soc. chim.*, (4), 13, 402, 1042, 1913.

[4] In the event of antimony or tin being present with the molybdenum, the mixture should be evaporated to dryness with phosphoric acid before it is treated with the sulphuric acid— R. Fresenius, *Qualitative Chemical Analysis*, London, 185, 1897. For the sulphuric acid test, see H. Schönn, *Zeit. anal. Chem.*, 8, 379, 1869; O. Maschke, *ib.*, 12, 383, 1873; *Arch. Pharm.*, (3), 6, 125, 1874; F. von Kobell, *Zeit. anal. Chem.*, 14, 317, 1875; *Charakteristik der Mineralien*, Nuremberg, 109, 1831; *Grundzüge der Mineralogie*, Nuremberg, 284, 1838; P. Truchot, *Ann. Chim. anal.*, 10, 254, 1905.

water bath and treat the cold, dry residue with concentrated ammonia solution until the reaction is strongly alkaline; add 3-4 per cent. hydrogen peroxide solution. If molybdic acid is present, a pale rose to cherry red coloration of ammonium permolybdate is obtained, depending on the amount of molybdic acid present. The test is exceedingly delicate, being sensitive to 0·006 mgrm. of molybdenum.[1]

(4) *Xanthic acid test.*— Add a trace of solid potassium xanthate to the solution to be tested and then acidify with a mineral acid. Molybdenum is indicated by the appearance of a red colour, the intensity of which varies as the amount of molybdenum present. The test is said to show the presence of 0·00064 mgrm. of molybdenum per c.c.[2]

Tungsten.—(1) The residue of tungsten and sulphur indicated above, or tungstic oxide itself, gives a blue solution when digested with a little zinc in the presence of hydrochloric or sulphuric acid. The test is made more sensitive by using the substance to be tested in a solid form. For example, the dry solid is moistened with a drop of hydrochloric acid and then rubbed with a piece of iron or aluminium— strong oxidising agents, *e.g.* chromates, chlorates, nitrates, must be absent. The production of the blue coloration is not prevented by carbonaceous matter, metallic oxides, sulphur or calcium fluoride.[3] (2) Stannous chloride gives a yellow precipitate with a soluble tungstate [4]; if the solution be acidified with hydrochloric acid and boiled, a blue colour is formed. (3) *Defaçqz's test.*[5] Heat a mixture of the oxide with four or five times its weight of potassium bisulphate and a few drops of sulphuric acid in a platinum capsule. Add enough sulphuric acid to prevent the mixture solidifying when it cools. On cooling, add a drop of this solution to a trace of phenol; if tungsten be present, an intense red colour is developed; if hydroquinone be used in place of phenol, an amethyst-violet coloration is formed with concentrated solutions, and a rose colour with dilute solutions.[6] Titanium and vanadium interfere with the test.

Columbium and Tantalum.—Digest the insoluble residue,[7] indicated above,

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[1] P. G. Melikoff, *Journ. Russ. Phys. Chem. Soc.*, **44**, 608, 1912; A. Komarowsky, *Chem. Ztg.*, **37**, 957, 1913. For the detection of molybdenum in coal ash, see A. Jorissen, *Bull. Soc. chim. Belg.*, **27**, 21, 1913.

[2] M. Siewert, *Zeit. ges. Naturw.*, **23**, 5, 1864; J. Koppel, *Chem. Ztg.*, **43**, 777, 1919; S. L. Malowan, *Zeit. anorg. Chem.*, **108**, 73, 1919.

[3] G. Torossian, *Amer. Journ. Science*, (4), **38**, 537, 1914; M. L. Hartmann, *Pahasapa Quart., S. Dakota School of Mines*, **5**, 23, 1916.

[4] Fuse the residual oxide with an excess of sodium carbonate, and take the mass up with water to get a soluble sodium tungstate—M. L. Hartmann, *Eng. Min. World*, **43**, 1021, 1915; *Chem. News*, **114**, 27, 45, 1916; R. F. Heath, *Chem. Trade Journ.*, **66**, 629, 1920; F. Feigl and P. Krumholz, *Angew. Chem.*, **45**, 674, 1932.

[5] E. Defaçqz (*Compt. rend.*, **123**, 308, 1896; *Chem. News*, **74**, 88, 1896) claims that this reaction will indicate the presence of between 0·0000025 and 0·000002 grm. of tungsten, whereas the blue colour developed by zinc and hydrochloric acid will only detect 0·001 grm. J. Moir, *Journ. Chem. Met. Min. Soc. S. Africa*, **16**, 191, 1916.

[6] G. Heyne, *Zeit. angew. Chem.*, **44**, 237, 1931. For quinine and strychnine, see F. Scheibler, *Journ. prakt. Chem.*, (1), **80**, 204, 1860. For hydrazine, pyrogallol and pyrocatechol, see J. Moir, *Journ. Chem. Met. Min. Soc. S. Africa*, **16**, 191, 1916. For the detection of tungsten by alkali thiocyanates and stannous chloride, see N. A. Tananaev and G. A. Pantchenko, *Journ. Russ. Phys. Chem. Soc.*, **61**, 1051, 1929. See also J. A. M. van Liempt, *Zeit. anorg. Chem.*, **122**, 236, 1922. For the colorimetric determination of tungsten, see A. Travers, *Compt. rend.*, **166**, 146, 1918; R. F. Heath, *Chem. Trade Journ.*, **66**, 629, 1920; A. Petrovskii, *Zeit. anal. Chem.*, **77**, 268, 1929; *Journ. Chem. Ind. (Moscow)*, **7**, 905, 1930; F. Feigl and P. Krumholz, *Angew. Chem.*, **45**, 674, 1932; S. Fernjančič, *Zeit. anal. Chem.*, **97**, 332, 1934.

[7] Antimony can be detected in the residue by fusion with potassium cyanide. Wash. Digest the insoluble matter with hydrochloric acid and a crystal of potassium chlorate. The antimony passes into solution. The washed residue is treated as described in the text.

in a platinum capsule with hydrofluoric acid in *slight* excess; add a saturated solution of potassium fluoride. Evaporate the solution to a very small volume. Let the solution cool slowly. If acicular rhombic crystals of potassium heptafluotantalate (fig. 100) separate, tantalum is present; if monoclinic plates of potassium oxypentafluocolumbate separate (fig. 101), columbium is also present. A good hand lens is a convenient means of recognising the crystals if they are small. It must be added that isomorphous potassium fluotantalate, K_2TaF_7, and potassium fluocolumbate, K_2CbF_7, separate from concentrated solutions of hydrofluoric acid,[1] but if an excess of hydrofluoric acid be not present, the solution containing columbium alone furnishes the plates of oxypentafluocolumbate, $K_2CbOF_5.H_2O$. By boiling dilute aqueous solutions of both salts hydrolysis occurs and tantalum and columbium oxyfluorides are formed. The latter is much more soluble than the former, so that the appearance of a turbidity when dilute aqueous solutions of the two salts are boiled enables small traces of tantalum to be detected in the presence of columbium.

Fig. 100.—Potassium Heptafluotantalate— K_2TaF_7.

Pick out a few of the acicular crystals and heat them on the lid of a platinum crucible with diluted sulphuric acid (sp. gr. 1·29) until the acid fumes strongly, so as to drive off the hydrofluoric acid. Treat the cold mass with an excess of water in a small glass capsule and boil the solution so as to precipitate the tantalic oxide. The precipitate dissolves in an excess of hydrochloric acid, giving an opalescent solution. Metallic zinc along with hydrochloric acid does not colour the solution; tannic acid with a drop of the solution gives a light yellow precipitate if tantalum be present.[2] If a few of the crystals of either potassium heptafluocolumbate or potassium oxypentafluocolumbate be treated in a similar way, and the precipitate dissolved in sulphuric acid, metallic zinc will give a blue coloration[3]; and tannic acid, an orange-red coloration.[4]

Fig. 101.—Potassium Oxypentafluocolumbate —$K_2CbOF_5.H_2O$.

Schoeller and Powell's Method.—This test[5] is applicable only in the absence of titanium, but a little zirconium does not interfere. Fuse 0·05 to 0·2 grm. of the sample with potassium pyrosulphate in a silica crucible. Dissolve the cold melt in 50 c.c. of a concentrated boiling solution of ammonium oxalate and test a few c.c. of the solution for titanium with hydrogen peroxide. If titanium is absent, boil the remainder of the solution with 0·2 to 0·3 grm. of tannin and then add 0·5N-ammonia, drop by drop, until a flocculent precipitate is formed. If this precipitate is pale to bright yellow, tantalum alone is present;

[1] The form of the crystals is also modified by the nature of the mother liquid and the temperature of crystallisation—C. Marignac, *Bibl. Univ. Arch. Genève*, **23**, 249, 1865; *ib.*, **26**, 89, 1866; *Œuvres Complètes*, Genève, **2**, 258, 334, 1894.

[2] Tungstic oxide under similar conditions gives a brown precipitate with tannic acid.

[3] See above for a blue coloration with tungstic acid under similar conditions.

[4] Molybdic acid gives an orange-red coloration with tannic acid—M. E. Pozzi-Escot, *Compt. rend.*, **138**, 200, 1904; vanadic acid, a blue coloration—C. Matignon, *ib.*, **138**, 82, 1904. Concentrated sulphuric acid solutions of columbic acid give characteristic colours with certain phenols, while tantalic acid gives only yellow colours—J. Moir, *Journ. Chem. Met. Min. Soc. S. Africa*, **16**, 189, 1916.

[5] A. R. Powell and W. R. Schoeller, *Analyst*, **50**, 494, 1925.

if it is orange to red, columbium is present [1] and tantalum is either absent or present in subordinate amounts. In the latter case, to ascertain the absence or presence of tantalum the precipitate is filtered off, washed, rinsed back and boiled with 25 c.c. of the ammonium oxalate solution. Redissolve the precipitate in 1·0N-sulphuric acid, to the clear solution add 0·1 to 0·2 grm. of tannin, boil and add 0·5N-ammonia, drop by drop, until a flocculent precipitate again forms. A pure yellow colour shows the presence of tantalum, but if only traces of this element are present the red colour of the columbium-tannin complex will obscure it. Hence the precipitate must again be filtered off and the procedure repeated until such time as the yellow tantalum colour is obtained or the absence of this element is confirmed.

§ 214. The Determination of Tungsten as Tungsten Trioxide.

If the substance under investigation can be decomposed by an acid,[2] tungsten trioxide—WO_3—will remain as an insoluble yellow powder. Repeated evaporation of a soluble tungstate (say, three times) with nitric acid or hydrochloric acid, washing and baking at 110° to 120° will render the tungstic oxide insoluble in acids. The dry mass is moistened with concentrated nitric acid, and after a 15 minutes' digestion add, say, 20 c.c. of a hot 5 per cent. solution of ammonium nitrate. Filter.[3] Wash with the 5 per cent. ammonium nitrate solution acidified with a few drops of concentrated nitric acid until all the alkali is removed. Dry. The filter-paper must be ignited separately to avoid reduction; hence, transfer the powder to a watch-glass and ignite the filter-paper in a weighed porcelain crucible, then transfer the powder carefully from the watch-glass to the crucible and ignite until the greenish tinge passes to a clear yellow. If the green colour persists, add a couple of drops of concentrated nitric acid and repeat the ignition.[4] Weigh the ignited mass as tungstic oxide—WO_3.

Unlike the corresponding molybdenum oxide, this oxide can be calcined at the highest temperature of a Bunsen burner without fear of appreciable loss by volatilisation. If the ignition be conducted over a blast, a 20 minutes'

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[1] The reduction of columbium pentoxide, Cb_2O_5, to a strongly coloured lower oxide can be used to detect traces of columbium in the presence of tantalum.—W. B. Giles, *Chem. News*, **95**, 1, 1907; E. Meimberg, *Zeit. angew. Chem.*, **26**, 83, 1913; O. Ruff and F. Thomas, *Zeit. anorg. Chem.*, **156**, 213, 1926; I. Wada and S. Kato, *Sci. Papers Inst. Phys. Chem. Research (Tokyo)*, **6**, 227, 1927; J. Moir, *Journ. Chem. Met. Min. Soc. S. Africa*, **16**, 189, 1916.

[2] C. W. Scheele, 1781—*Opuscula Chemica et Physica*, Lipsiæ, **2**, 119, 1789—used nitric or hydrochloric acid; F. Marguerite (*Ann. Chim. Phys.*, (3), **17**, 475, 1846), dilute sulphuric acid. C. Scheibler, *Journ. prakt. Chem.*, (1), **83**, 273, 1861; *Chem. News*, **6**, 182, 1862; R. Hermann, *Zeit. anal. Chem.*, **51**, 736, 1912; R. Fieber, *Chem. Ztg.*, **36**, 334, 1912; S. Zinberg, *Zeit. anal. Chem.*, **52**, 529, 1913; H. Arnold, *Zeit. anorg. Chem.*, **88**, 74, 1914; M. L. Hartmann, *Chem. News*, **114**, 27, 45, 1916; L. Löwy, *Zeit. angew. Chem.*, **32**, 379, 1919; F. W. Foote and R. S. Ransom, *Eng. Min. Journ.*, **105**, 836, 1918; H. Corti, *Anal. Soc. Quim. Argentina*, **5**, 308, 1917; I. Koppel, *Chem. Ztg.*, **48**, 801, 1924; J. A. M. van Liempt, *Zeit. anorg. Chem.*, **127**, 215, 1923; *Rec. Trav. chim.*, **43**, 30, 1924; E. Cremer and B. Fetkenheuer, *Wiss. Veröff. Siemens-Konz.*, **5**, 199, 1927; I. Kassler, *Zeit. anal. Chem.*, **76**, 113, 1929; H. Mende, *Chem. Ztg.*, **53**, 178, 1929; W. Brüggemann, *ib.*, **53**, 927, 947, 1929; K. Swoboda and R. Horny, *Zeit. anal. Chem.*, **80**, 271, 1930; N. S. Singalovskii and P. M. Porchunov, *Redkie Metal*, **2**, 35, 1933; *Chem. Zentr.*, (1), 424, 1934. See J. W. Mallet (*Journ. Chem. Soc.*, **28**, 1228, 1875; *Chem. News*, **31**, 276, 1875) for the solubility of tungstic acid when an excess of concentrated hydrochloric acid is added to an alkali tungstate.

[3] A Gooch crucible can be used if the precipitate is not to be subjected to further treatment.

[4] If the alkalies have not all been removed in the washing, the green tinge cannot be always removed by this treatment.

ignition is said to have caused a loss of up to 7 per cent. Thus, tungstic oxide weighing 0·3007 grm. was reduced after 20 minutes' blasting to 0·2872 grm.[1]

§ 215. The Gravimetric Determination of Tungsten— Berzelius' Process.

A concentrated alkaline solution of the tungstate is neutralised with nitric acid and a few drops of nitric acid in excess are added. The solution is therefore feebly acid. Add an excess of mercurous nitrate [2] solution. Agitate the solution. Then add ammonia, drop by drop, with constant stirring,[3] until a brown precipitate separates. Heat the solution to boiling. Let the precipitate settle. Filter and wash with water containing 2 per cent. of mercurous nitrate. Dry, ignite and weigh the residual tungstic oxide as WO_3.[4]

§ 216. The Separation of Tungsten and Silica.

The separation of tungstic oxide and silica presents some difficulties because, if an excess of tungstic oxide be present, a complex, $SiO_2.12WO_3$, will be produced.[5] The presence of mineral acids prevents the formation of

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[1] H. L. Wells and F. J. Metzger, *Journ. Amer. Chem. Soc.*, 23, 356, 1901.

[2] MERCUROUS NITRATE SOLUTION.— Digest 60 grms. of pure mercury with 25 c.c. of nitric acid (sp. gr. 1·4) and 75 c.c. of water on a water bath for about 1½ hours. Let the mixture stand overnight. Dilute the solution to 400 c.c. (0·75E). The addition of about 20 c.c. usually suffices for the precipitation. The solution should give no residue when evaporated to dryness and the mercurous nitrate volatilised.

[3] Some prefer to add the mercurous nitrate solution directly to the alkaline solution. O. F. von Pfordten (*Liebig's Ann.*, 222, 152, 1883; *Chem. News*, 50, 18, 1884; *Zeit. anal. Chem.*, 24, 92, 1885) says the mercurous nitrate may be added to the neutral solution if it is free from carbon dioxide.

[4] J. J. Berzelius, *Schweigger's Journ.*, 16, 476, 1816; W. W. Hutchin, *Analyst*, 36, 398, 1911; E. Bagley and H. Brearley, *Chem. News*, 82, 270, 1900; L. Desvergnes, *Ann. Chim. anal.*, 9, 321, 1904; W. Gibbs, *Amer. Chem. Journ.*, 1, 219, 1879; C. de Marignac, *Ann. Chim. Phys.*, (3), 69, 84, 1863; M. Wunder and A. Schapira, *Ann. Chim. anal.*, 18, 257, 1913; E. Dittler and A. von Graffenreid, *Chem. Ztg.*, 40, 681, 1916; V. I. Spitzin, *Journ. Russ. Phys. Chem. Soc.*, 60, 1229, 1928; *Zeit. anal. Chem.*, 75, 443, 1928; O. R. Sweeney, *Journ. Amer. Chem. Soc.*, 38, 2377, 1916; H. W. Hutchin and F. J. Fouks, *Inst. Min. Met.*, 18, 425, 1909. Instead of mercurous nitrate, lead acetate is sometimes used—*e.g.* T. M. Chatard, *Amer. J. Science*, (3), 4, 416, 1871; *Chem. News*, 24, 175, 1871; F. A. Bernoulli, *Pogg. Ann.*, 111, 573, 1860; *Chem. News*, 5, 116, 1862; H. Brearley, *ib.*, 79, 64, 1899; F. Ibbotson and H. Brearley, *ib.*, 80, 293, 1899; E. Zettnor, *ib.*, 16, 12, 1867; J. S. de Benneville, *Journ. Amer. Chem. Soc.*, 19, 377, 1897. Organic precipitating agents have been recommended, *e.g.* quinine acetate or sulphate (J. Lefort, *Journ. Pharm. Chim.*, (3), 4, 221, 326, 1881; *Chem. News*, 45, 57, 1882; A. Jílek and J. Lukas, *Coll. Czech. Chem. Comm.*, 1, 263, 1929; *Chem. Listy*, 24, 73, 1930); cinchonine (H. Cremer, *Eng. Min. Journ.*, 59, 345, 1895; H. Lavers, *Proc. Austral. Inst. Min. Met.*, 101, 1921; H. Yagoda and H. A. Fales, *Journ. Amer. Chem. Soc.*, 58, 1494, 1936); tannin (W. R. Schoeller and C. Jahn, *Analyst*, 52, 504, 1927; L. Moser and W. Blaustein, *Monats.*, 52, 350, 1929); benzidine (G. von Knorre, *Ber.*, 38, 783, 1905; *Zeit. anal. Chem.*, 47, 37, 1908; *Stahl Eisen*, 28, 984, 1908; V. K. Kantschev, *Journ. Russ. Phys. Chem. Soc.*, 46, 729, 1914; B. G. Mokeev, *Uchenuie Zapiski Kazan Gosudarst Univ.*, 90, 1022, 1932; H. Wdowiszewski, *Chem. Ztg.*, 34, 1365, 1910; F. W. Hinrichsen, *Mitt. König. Materialprüf. Gross. Lichter. West.*, 25, 308, 1907; L. Moser and K. Schmidt, *Monats.*, 47, 313, 1926)—also used for the separation of tungsten from phosphoric acid; α-naphthylamine (M. Tschilikin, *Ber.*, 42, 1302, 1909). E. Kafka (*Zeit. anal. Chem.*, 52, 601, 1913) uses ψ-cumidine, tetramethyldiaminobenzophenone or tetramethyldiamino-diphenylmethane; A. Gutbier and G. L. Weise (*ib.*, 53, 426, 1914), "nitron," otherwise diphenylendoanilodihydrotriazole; and G. Dotreppe (*Bull. Soc. chim. Belg.*, 38, 385, 1929), phenylhydrazine hydrochloride. B. Mdivani (*Bull. Soc. chim.*, (4), 9, 122, 1911; E. E. Marbaker, *Journ. Amer. Chem. Soc.*, 37, 86, 1915) precipitates W_2O_5 by adding a solution of stannous chloride to a soluble tungstate.

[5] H. Hermann, *Zeit. anal Chem.*, 52, 557, 1913; L. Guglialmelli and U. Hordh, *Anal. Soc. Quim. Argentina*, 5, 81, 1917.

this substance but, once formed, it is exceedingly difficult to resolve into silica and tungstic oxide.

Hydrofluoric Acid Process.—This is best effected by the volatilisation of the silica—in the usual way—by treatment of the mixture with sulphuric and hydrofluoric acids [1] (page 149). Prolonged ignition is not always sufficient to drive off the last traces of sulphuric acid. In that case, a piece of pure solid ammonium carbonate in the crucible will remove the acid in question.[2] Wells and Metzger [3] have shown that Herting's assertion [4] that some tungstic oxide is volatilised by this treatment is unfounded. The mixture, however, should not be blasted, for the reason indicated above.

Ammonia Process.—The method [5] of separating tungstic oxide from silica based on the solubility of moist tungstic oxide in ammonia is not to be used if it can be avoided, since the silicic acid is slightly soluble in the same menstruum (page 165) or passes through the paper with the tungstic oxide, though this is said to be prevented by the addition of a little ammonium chloride to the ammonia used for washing out the tungstic oxide; but the error is relatively small. If the mixture be baked, so as to reduce the solubility of the silica, some of the tungstic oxide also becomes insoluble.[6]

Potassium Bisulphate Process.—The methods [7] of separation depending upon the fusion of tungstic oxide and silica with, say, 5 parts of potassium bisulphate, and subsequent digestion of the residue with ammonium carbonate or ammonium sulphide, $(NH_4)_2S$,[8] to dissolve the tungstic oxide, take no account of the slight solubility of silica in potassium bisulphate (page 167), and of the failure of these menstrua to dissolve all the tungstic oxide.[9] The errors are small, and the experimental results, at present, meet commercial requirements.[10]

Hydrogen Chloride Process.—Vanadium, molybdenum and tungsten can be separated from silica by passing hydrogen chloride over the mixture at a red heat.[11] The chlorides pass over into the receiver and silica remains quanti-

[1] J. S. de Benneville, *Journ. Amer. Chem. Soc.*, 19, 377, 1897; M. Wunder and A. Schapira, *Ann. Chim. anal.*, 18, 257, 1913; H. Arnold, *Zeit. anorg. Chem.*, 88, 333, 1914; C. F. van Duin, *Chem. Weekb.*, 14, 169, 1917; F. Kehrmann and B. Flürscheim, *Zeit. anorg. Chem.*, 39, 98, 1904.

[2] H. Rose, *Ausführliches Handbuch der analytischen Chemie*, Braunschweig, 2, 343, 1851; F. Kehrmann and B. Flürscheim, *Zeit. anorg. Chem.*, 39, 98, 1904.

[3] H. L. Wells and F. J. Metzger, *Journ. Amer. Chem. Soc.*, 23, 356, 1901; *Chem. News*, 83, 3, 1901; A. G. McKenna, *Proc. Eng. Soc. Pennsylvania*, 16, 119, 1900; *Eng. Min. Journ.*, 66, 607, 1898.

[4] O. Herting, *Zeit. angew. Chem.*, 14, 165, 1901; *Chem. News*, 84, 75, 1901.

[5] H. Bornträger, *Zeit. anal. Chem.*, 39, 361, 1900; J. Preusser, *ib.*, 28, 173, 1889; *Chem. News*, 60, 37, 1889; S. Kern, *ib.*, 35, 67, 1877; J. Parry and J. J. Morgan, *ib.*, 67, 260, 1893; A. Cobenzl, *Monats.*, 2, 259, 1881; J. S. de Benneville, *Journ. Amer. Chem. Soc.*, 19, 377, 1897; H. Cremer, *Eng. Min. Journ.*, 59, 345, 1895; H. F. Watts, *Chem. News*, 95, 19, 1907; L. and G. Campredon, *Ann. Chim. anal.*, 9, 41, 1904; L. Wolter, *Chem. Ztg.*, 34, 2, 1910; R. Namias, *Stahl Eisen*, 11, 757, 1891.

[6] H. Arnold, *Zeit. anorg. Chem.*, 88, 74, 1914.

[7] L. Schneider and F. Lipp, *Zeit. anal. Chem.*, 24, 292, 1885; *Chem. News*, 51, 297, 1885; R. Schöffel, *ib.*, 41, 31, 1880; *Ber.*, 12, 1866, 1879; O. Herting, *Zeit. angew. Chem.*, 14, 165, 1901; C. Marignac, *Ann. Chim. Phys.*, (4), 3, 6, 1864.

[8] H. Rose, *Pogg. Ann.*, 100, 146, 1857.

[9] R. D. Hall, *Journ. Amer. Chem. Soc.*, 26, 1235, 1904; E. F. Smith, *Proc. Amer. Chem. Soc.*, 44, 151, 1905.

[10] E. Defaçqz (*Compt. rend.*, 123, 823, 1896) separates tungsten and titanium by fusing the mass with potassium nitrate, mixed with one-fourth its weight of potassium carbonate. When the cold melt is extracted with water, titanium oxide remains insoluble, but the tungsten dissolves. G. Fenner (*Chem. Ztg.*, 42, 403, 1918) uses sodium peroxide as a flux.

[11] C. Friedheim and C. Castendyck, *Ber.*, 33, 1611, 1900; C. Friedheim and W. H. Henderson, *ib.*, 35, 3242, 1902; C. Friedheim, W. H. Henderson and A. Pinagel, *Zeit. anorg. Chem.*, 45, 396, 1905. Compare P. Jannasch and R. Leiste, *Journ. prakt. Chem.*, (2), 97, 141, 1918;

tatively in the platinum boat. The hydrogen chloride must be free from oxygen, or chlorine may be liberated and attack the platinum.

§ 217. The Separation of Tungsten and Tin.

Rose and Rammelsberg's Process.—Rose [1] has shown that stannic oxide may be removed from tungstic oxide by repeated ignition with ammonium chloride. The ammonium chloride reacts with the stannic oxide, forming volatile stannic chloride, while the tungstic oxide remains behind. Rammelsberg [2] recommends the following method of conducting the operation:—Mix the weighed residue from the hydrofluoric acid treatment with six to eight times its weight of ammonium chloride.[3] Place the covered crucible containing the mixed stannic and tungstic oxides in a larger crucible. The latter is covered with a lid. Heat the crucibles as long as vapours of ammonium chloride issue from the outer crucible. Repeat the treatment three times. The object of using two crucibles is to prevent the formation of a coat of stannic oxide on the outside of the smaller crucible. The stannic oxide is formed by a reaction between the vapours of stannic chloride which issue from the crucible and the moisture of the air. The contents of the inner crucible become green and finally almost black in colour. The yellow colour is restored when the small crucible is ignited while exposed to the air. If a fourth treatment with ammonium chloride gives the same weight as the third, it is assumed that all the stannic oxide has been driven off. The inner crucible is then ignited alone and finally weighed as indicated in § 214, page 441. The following numbers, by Rammelsberg himself, illustrate the accuracy of the process:—

Stannic oxide taken	.	.	.	0·6977	0·554 grm.
Tungstic oxide taken	.	.	.	0·7335	1·332 grm.
Tungstic oxide found	.	.	.	0·7355	1·337 grm.

Donath and Müllner's Process.—According to Rammelsberg,[4] Rose's method of reduction by heating a mixture of tin and tungsten oxides in a current of hydrogen and dissolving out the reduced tin with hydrochloric acid, is not very exact.[5] Donath and Müllner [6] obtained better results by mixing the two oxides

L. Moser and K. Schmidt, *Monats.*, **47**, 313, 1926; *Zeit. angew. Chem.*, **40**, 667, 1927. For treatment of the mixture of silica and tungstic oxide with standard sodium hydroxide, $WO_3 + 2NaOH = Na_2WO_4 + H_2O$, and back-titration with standard hydrochloric acid, using phenolphthalein as indicator, see F. Hundeshagen, *Chem. Ztg.*, **18**, 547, 1894; S. C. Lind and B. C. Trueblood, *Journ. Amer. Chem. Soc.*, **29**, 477, 1907; O. Herting, *Zeit. angew. Chem.*, **14**, 165, 1901; J. Ciochina, *Zeit. anal. Chem.*, **72**, 429, 1927.

[1] H. Rose, *Ausführliches Handbuch der analytischen Chemie*, Braunschweig, **2**, 352, 1871; W. P. Dexter, *Pogg. Ann.*, **92**, 335, 1854; E. Dittler and A. von Graffenreid, *Chem. Ztg.*, **40**, 681, 1916; M. Travers, *Compt. rend.*, **165**, 408, 1907. J. Ciochina (*Zeit. anal. Chem.*, **72**, 429, 1927) separates tin and tungstic oxides by digesting the mixture with a warm, concentrated solution of sodium tungstate in which the tungstic oxide dissolves. Prolonged digestion may dissolve part of the silica, if present, as silicotungstate. K. Agte, H. Becker-Rose and G. Heyne (*Zeit. angew. Chem.*, **38**, 1121, 1925) separate tin by electrolysis.

[2] C. Rammelsberg, *Pogg. Ann.*, **120**, 66, 1864; *Chem. News*, **9**, 25, 1864.

[3] The ammonium chloride must be tested to make sure that it yields no non-volatile constituents when heated in a platinum dish.

[4] C. Rammelsberg, *Pogg. Ann.*, **120**, 66, 1864; *Chem. News*, **9**, 25, 1864.

[5] For reduction by hydrogen between 600° and 900°, forming either a lower oxide or metal, see C. Marignac, *Ann. Chim. Phys.*, (4), **3**, 9, 1864; E. Defaçqz, *Compt. rend.*, **146**, 1319, 1908; **144**, 848, 1907; C. Friedheim, W. H. Henderson and A. Pinagel, *Zeit. anorg. Chem.*, **45**, 396, 1905. The process is recommended for the separation of tungstic oxide and silica by L. E. Rivot, *Ann. Chim. Phys.*, (3), **30**, 188, 1850; A. Hilger and H. Haas, *Ber.*, **23**, 458, 1890.

[6] E. Donath and F. Müllner, *Monats.*, **8**, 647, 1887; *Chem. News*, **59**, 73, 1889; E. Donath, *Zeit. angew. Chem.*, **19**, 473, 1906; H. Angenot, *ib.*, **19**, 956, 1906; J. Preusser, *Zeit. anal. Chem.*, **28**, 173, 1889.

with twice their weight of zinc dust, and, after 15 minutes' ignition in a covered crucible, dissolving up the residue by boiling with dilute hydrochloric acid (1 : 2). Add sufficient potassium chlorate to the cold solution to oxidise the blue tungsten oxide to the yellow oxide. Dilute the solution with 1·5 times its volume of water and, after 24 hours, filter, ignite and weigh the precipitate as WO_3. The tin can be determined in the filtrate by precipitation with hydrogen sulphide.

Electrolytic Process.—Tin can be separated from a solution containing the two sulphides in a mixture of sodium sulphide and hydroxide by using a current density of 1·7 to 0·5 ampere per square dm. with 1·7 to 2·3 volts at 50°-60°. The deposited tin is free from tungsten but contains traces of sulphur. With rotating electrodes 0·1 grm. is deposited in about an hour; with stationary electrodes, 4 hours. Molybdenum, if present, will contaminate the tin.[1]

§ 218. The Separation of Tungsten from Tin and Antimony— Talbot's Process.

Hallopeau[2] has shown that when a mixture of soluble antimony and tungsten salts is treated with mercurous nitrate, a mercurous antimonio-tungstate—$3HgSbO_3.2WO_3$—is precipitated, and this, on ignition, furnishes antimony tetroxide and tungsten trioxide. When antimony is present, the separation, according to Hallopeau, is best effected by Talbot's process for the separation of tungsten and tin.[3]

In Talbot's process[4] the mixed oxides[5] are fused with potassium cyanide as indicated on page 268. If too little potassium cyanide be used, a black residue containing tungsten may be formed. One part of the mixed oxides with 12 parts by weight of potassium cyanide usually suffices. The tin and antimony remain behind as metals; the alkali tungstate formed at the same time passes into solution when the mass is leached with water. Filter and wash. The aqueous solution is boiled with an excess of nitric acid to drive off the volatile cyanogen compounds.[6] The tungstate is then precipitated by the usual process. If phosphorus be present, it will be found in the solution with the tungsten. The separation is described below. The metallic bead is dissolved in acid and analysed in the ordinary manner—mixture of tin and antimony.[7]

[1] W. D. Treadwell, *Elecktrochem. Zeit.*, 19, 381, 1913; compare A. Jilek and J. Lukas, *Chem. Listy*, 18, 205, 1924.

[2] L. A. Hallopeau, *Bull. Soc. chim.*, (3), 17, 170, 1897; A. Travers, *Compt. rend.*, 165, 408, 1917.

[3] Hallopeau found that the fusion of the mixture of antimony and tungsten oxides with sodium hydroxide and extraction of the sodium tungstate with alcohol is not satisfactory. Some sodium antimonate passed into solution.

[4] J. H. Talbot, *Amer. J. Science*, (2), 50, 244, 1870; *Chem. News*, 22, 229, 1870; R. Helmhacker, *Eng. Min. Journ.*, 60, 153, 1896; B. Setlik, *Chem. Ztg.*, 13, 1474, 1889; *Chem. News*, 61, 54, 1890; E. D. Desi, *Journ. Amer. Chem. Soc.*, 19, 239, 1897.

[5] Tin and tungsten; antimony and tungsten; or tin, antimony and tungsten.

[6] Note these poisonous fumes make it necessary to perform the operation under a hood.

[7] If any antimony adheres tenaciously to the walls of the crucible, remove the metal by treatment with acids; or, if antimony or tin alone be present, wash the crucible, dry and weigh. Add some ammonium chloride and heat the crucible to redness; the antimony volatilises. The loss in weight represents the amount of metal which adhered to the crucible.

§ 219. The Separation of Tungsten from Arsenic and Phosphorus—Kehrmann's Process.

The separation of arsenic and tungsten is exceedingly difficult, because part of the arsenic is retained very tenaciously by the tungsten as a complex salt—arsenotungstate.   The distillation process (page 279) for arsenic does not give satisfactory results in the presence of tungsten.[1]   The following process is due to Kehrmann.[2]   The same process can be applied, *mutatis mutandis*, to the separation of tungsten and phosphorus.[3]

Fuse between 1 and 2 grms. of the sample with twice as much sodium hydroxide as is needed to combine with the arsenic oxide.   Add enough water to dissolve the resulting cake.   Boil the solution in an Erlenmeyer's flask for about half an hour.   Cool.   Add three times as much ammonium chloride as is needed to form chlorides with the alkalies present.   Add ammonia—about one-fourth the volume of the solution under investigation—and cold magnesia mixture.   In about 12 hours the precipitate of ammonium magnesium arsenate is filtered and washed with a solution of ammonia and ammonium nitrate (page 284).   It is advisable to dissolve the precipitate in dilute acid, repeat the precipitation a number of times [4] and treat the precipitate as indicated on page 284.

The tungstic acid is separated from the combined filtrates by evaporation with nitric acid (page 441).   The precipitate is washed with a mixture of nitric acid and ammonium nitrate and weighed as indicated on page 441.   It is difficult to get the tungsten quite free from magnesia.   Gooch [5] first determines the total weight of tungsten and arsenic, then separates the tungsten by the mercurous nitrate process and estimates the arsenic by difference.

§ 220. The Precipitation of Molybdenum as Sulphide.

Molybdenum is precipitated from an acid solution as sulphide—MoS_2—in the hydrogen sulphide group.   It is almost impossible to effect complete separa-

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[1] C. Friedheim and P. Michaelis, *Ber.*, **28**, 1414, 1895.   S. Hilpert and T. Dieckmann (*Ber.*, **46**, 152, 1913; **47**, 2444, 1914) distil a mixture of the two acids with 15 grms. of cuprous bromide and 150 c.c. of hydrochloric acid (sp. gr. 1·16) after the addition of a fairly large quantity of phosphoric acid.   The latter forms a complex with the tungstic acid and on distillation the whole of the arsenic is found in the distillate.   Molybdenum and vanadium can be separated similarly from arsenic, but the addition of phosphoric acid is unnecessary. See also O. R. Sweeney, *Journ. Amer. Chem. Soc.*, **38**, 2377, 1916.   K. Agte, H. Becker-Rose and G. Heyne (*Zeit. angew. Chem.*, **38**, 1121, 1925) separate arsenic by distillation with a mixture of methyl alcohol, hydrochloric acid and pyrogallol.

[2] F. Kehrmann, *Liebig's Ann.*, **245**, 56, 1888; *Ber.*, **20**, 1813, 1887.   F. W. Hinrichsen (*Mitt. Königl. Materialprüfungsamt.*, **28**, 229, 1910), for the separation of phosphorus (P_2O_5) and tungsten (WO_3), recommends the mercurous nitrate process (page 442); the ignited precipitate is fused with alkali carbonate.   The phosphorus can be precipitated from the aqueous extract of the cold cake by first precipitating the phosphates with magnesia mixture and, after taking up the precipitate with nitric acid, reprecipitating (page 675).   See also H. Arnold, *Zeit. anorg. Chem.*, **88**, 333, 1914; K. Agte, H. Becker-Rose and G. Heyne, *l.c.*

[3] For the separation of phosphorus from tungsten, see G. W. Gray and J. Smith, *Journ. Iron Steel Inst.*, **99**, 585, 1919; T. E. Rooney and L. M. Clark, *ib.*, **113**, 457, 1926; C. M. Johnson, *Journ. Ind. Eng. Chem.*, **5**, 297, 1913; G. E. F. Lundell and H. B. Knowles, *ib.*, **15**, 44, 171, 1923.   For phosphorus in scheelite, see E. W. Hagmaier, *Met. Chem. Eng.*, **12**, 620, 1914; W. Dewar, *Mining Mag.*, **16**, 252, 1917; K. Agte, H. Becker-Rose and G. Heyne, *l.c.*

[4] The arsenic and phosphorus can be separated in the usual way if they are present together.

[5] F. A. Gooch, *Proc. Amer. Acad.*, **16**, 134, 1881; *Amer. Chem. Journ.*, **1**, 412, 1879; W. Gibbs, *ib.*, **7**, 337, 1885; H. Bullnheimer, *Chem. Ztg.*, **24**, 870, 1900; *Chem. News*, **85**, 184, 1902.

tion in a hydrochloric acid solution. The separation is more complete in sulphuric acid solutions, but even then the separation is not satisfactory in a reasonable time. For instance, a solution of ammonium molybdate acidified with five volumes of concentrated sulphuric acid was saturated with hydrogen sulphide. The solution was filtered after it had been allowed to settle for an hour, and the filtrate was again treated with hydrogen sulphide. This sequence of operations was repeated in all five times. A little molybdenum sulphide was precipitated each time. Hence, *molybdenum, in acid solutions, is but imperfectly precipitated by hydrogen sulphide at atmospheric pressures.*[1]

If a pressure bottle be used, the results are satisfactory.[2] The pressure flask (page 276) of 300, 500 or 1000 c.c. capacity is closed by a ground-glass plate.[3] About 250 c.c. of the solution are placed in the flask and saturated with hydrogen sulphide by passing a rapid stream of gas through the solution.[4] Dilute the solution to about 500 c.c. with water saturated with hydrogen sulphide. The flask is then placed in a cold water bath and gradually heated to boiling. The bath is kept at that temperature for about an hour. Let the bottle cool; empty the contents into a beaker; and wash the bottle with dilute acid (sulphuric acid 1, water 50) saturated with hydrogen sulphide. Let the precipitate settle. Filter and wash the precipitate with the dilute acid saturated with hydrogen sulphide. An alternative method, which works well, is to make the solution ammoniacal, add a slight excess of ammonium monosulphide and then acidify with sulphuric acid. Warm to coagulate the precipitated molybdenum sulphide, filter and wash as above.[5]

If several members of the hydrogen sulphide group be present, the precipitated sulphides are digested with ammonium monosulphide for a couple of hours, when molybdenum, arsenic, antimony and tin,[6] if present, will pass into solution. Vanadium and uranium, if present, are not precipitated by the above treatment. Tungsten is partly precipitated, but not if 3 to 5 grms. of tartaric acid be added to the solution before passing the hydrogen sulphide.[7] If much iron be present, an appreciable quantity may be carried down with the sulphides. For instance, a solution containing 0·1076 grm. of iron with

[1] E. Döhler, *Chem. Ztg.*, **24**, 537, 1900; *Chem. News*, **82**, 294, 1900; F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, **2**, 183, 1911; F. van Dyke Cruser and E. H. Miller, *Journ. Amer. Chem. Soc.*, **26**, 675, 1904; *Chem. News*, **90**, 204, 218, 1904; H. Traube, *Neues Jahrb. Min., B.B.*, **7**, 232, 1891; C. Friedheim and R. Meyer, *Zeit. anorg. Chem.*, **1**, 76, 1892; E. Farber, *Chem. Ztg.*, **51**, 171, 1927; H. Mende, *ib.*, **53**, 178, 1929; H. C. Weirick and C. H. McCollam, *Heat. Treat. Forg.*, **16**, 1145, 1155, 1930; J. Stěrba-Böhm and J. Vostřebal, *Zeit. anorg. Chem.*, **110**, 81, 1920.

[2] S. Zinberg, *Zeit. anal. Chem.*, **52**, 529, 1913; A. V. Fuller, *Journ. Ind. Eng. Chem.*, **9**, 793, 1917; A. E. Stoppel, C. F. Sidener and P. H. M. P. Brinton, *Chem. News*, **130**, 353, 1925; E. Cremer and B. Fetkenheuer, *Wiss. Veröff. Siemens-Konz.*, **5**, 199, 1927; K. Swoboda and R. Horny, *Zeit. anal. Chem.*, **80**, 271, 1930; E. Wendehorst, *ib.*, **73**, 452, 1928.

[3] An empty "citrate of magnesia" bottle makes a good pressure flask for the operation.

[4] A fast current of gas causes less trouble by the sticking of the sulphide to the walls of the tube than a slow current of the gas. B. Herstein (*Bull. U.S. Dept. Agric. Chem.*, **150**, 44, 1912) uses 0·75 c.c. thioacetic acid per 0·1 grm. MoO₃ in place of hydrogen sulphide.

[5] W. Hoepfner and O. Binder, *Chem. Ztg.*, **42**, 315, 564, 1918; A. E. Stoppel, C. F. Sidener and P. H. M. P. Brinton, *Chem. News*, **130**, 353, 1925; I. Koppel, *Chem. Ztg.*, **48**, 801, 1924; W. Hartmann, *Zeit. anal. Chem.*, **67**, 152, 1925; E. Wendehorst, *ib.*, **73**, 452, 1928; W. Werz, *ib.*, **80**, 109, 1930.

[6] Selenium, tellurium and germanium, if present, will be found mainly in the ammonium sulphide solution.

[7] H. Rose, *Handbuch der analytischen Chemie*, Braunschweig, **2**, 358, 1871; H. Yagoda and H. A. Fales, *Journ. Amer. Chem. Soc.*, **58**, 1494, 1936. If tungstic oxide be present, most of it will be found in the residue with the silica. The silica is driven off by means of hydrofluoric acid (page 149), and the residue is treated as indicated on page 441 for WO₃.

different amounts of molybdenum in the same solution gave the following numbers—

| Molybdenum | . | 0·00492 | 0·00984 | 0·02460 | 0·04921 grm. |
| Ferric oxide | . | 0·0001 | 0·0002 | 0·0003 | 0·0005 grm. |

when the iron was separated from the precipitated molybdenum sulphide and weighed as ferric oxide. To recover iron from the molybdenum sulphide, dissolve the washed precipitate in a mixture of 10 c.c. of hydrochloric acid, 5 c.c. of nitric acid and 10 c.c. of concentrated sulphuric acid. Evaporate the solution until copious fumes of sulphur oxides are evolved. Cool. Add 50 c.c. of water and an excess of ammonia. The ferric hydroxide which separates may be filtered off.

If no other member of the ammonium sulphide sub-group be present, the warm solution is acidified with hydrochloric or sulphuric acid, and the reddish-yellow solution is boiled to drive off the hydrogen sulphide.[1] Filter and wash the brown precipitate with hot water acidified with hydrochloric (or sulphuric) acid and saturated with hydrogen sulphide. The precipitated molybdenum sulphide may now be treated in several different ways—gravimetric or volumetric.

Arsenic can be separated from molybdenum by the magnesia-mixture process described on page 282. Two or three precipitations are needed to obtain a precipitate of ammonium magnesium arsenate free from molybdenum.[2]

Tin sulphide can be separated by treatment with a solution of oxalic acid slightly acidified with hydrochloric acid, as indicated in Clarke's process (page 298).

§ 221. The Gravimetric Determination of Molybdenum as Oxide, and as Sulphide.

Determination of Molybdenum as Oxide.—If molybdenum alone be present, the sulphide can be conveniently transformed into the oxide by washing it first with dilute sulphuric acid (1 : 20), and then with alcohol until all the acid is removed. The moist filter-paper is placed in a large porcelain crucible and dried in an air bath. Carbonise the filter-paper over a small flame while the cover is on the crucible. Remove the cover. Burn the carbon from the sides of the crucible with as small a flame as possible and raise the temperature of the crucible very gradually. When the evolution of sulphur dioxide has ceased, cool. Add a little mercuric oxide suspended in water. Stir up the mixture in the crucible and evaporate to dryness on the water bath. Drive off the mercuric oxide by gentle ignition.[3] Weigh as molybdenum trioxide— MoO_3. The oxide should be white, not tinted blue.

Errors.—The chief difficulties in determining molybdenum as trioxide arise from the tendency of the sulphide to oxidise so violently as to project particles from the crucible during calcination; and the tendency of the oxide to volatilise

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[1] F. E. Zenker, *Journ. prakt. Chem.*, (1), **58**, 257, 1853.

[2] Arsenic can also be separated by the distillation process indicated on page 279. In order to avoid the introduction of large amounts of iron, C. Friedheim and P. Michaelis (*Ber.*, **28**, 1414, 1895) recommend distillation from methyl alcohol saturated with hydrochloric acid.

[3] The mercuric oxide helps to burn off the carbon and also assists in the removal of some sulphur oxide. O. Binder (*Chem. Ztg.*, **42**, 255, 1918), after a preliminary ignition of the sulphide, treats the residue with nitric acid, evaporates to dryness and dissolves the mass in ammonia. The solution is reprecipitated with nitric acid, again evaporated and ignited.

at comparatively low temperatures.[1] When the sulphide is calcined, a blue oxide is first formed. This contains less oxygen than the trioxide, and the calcination must therefore be continued until the mass in the crucible is white, not blue, when cold. This requires so prolonged a calcination that the oxide begins to volatilise before all the blue oxide is transformed into trioxide and the weight is constant. For instance, Collett and Eckardt[2] roasted the sulphide[3] at a low temperature and weighed the crucible and contents after the lapse of different intervals of time. The results are illustrated in fig. 102.
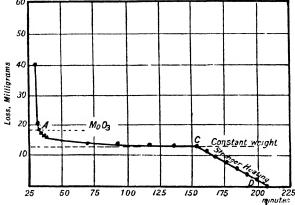
FIG. 102. — Loss in Weight during the Ignition of Molybdenum Sulphide.

The curve shows that the weight decreases rapidly as the sulphide is oxidised. Immediately after all has been converted into the trioxide (A, fig. 102), the oxide continues to lose weight but, after about a couple of hours, the weight remains nearly constant, although the weight of the substance is really 1–2 per cent. less than it should be. This is due to the volatilisation of the oxide,[4] although the oxide in the crucible still has a blue tint. If the temperature of calcination be raised, the loss by volatilisation is greater. This is illustrated by the quick descent of the curve CD (fig. 102). With some practice, it is possible to conduct the operation quite satisfactorily. Collett and Eckardt, however, consider that the process should be abandoned, and the molybdenum weighed as sulphide.

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[1] E. Collett and M. Eckardt, *Chem. Ztg.*, **33**, 968, 1909; L. A. Congdon and L. V. Rohner, *Chem. News*, **128**, 118, 1924. W. Treadwell (*Elektrochem. Zeit.*, **19**, 219, 1913), K. Wolf (*Zeit. angew. Chem.*, (1), **31**, 140, 1918) and K. Swoboda and R. Horny (*Zeit. anal. Chem.* **80**, 271, 1930) state that sublimation occurs above 450°, and recommend that the ignition should be carried out at 400°–450°. P. H. M. P. Brinton and A. E. Stoppel (*Journ. Amer. Chem. Soc.*, **46**, 2454, 1924) ignite at a temperature not exceeding 600°. M. Seligsohn (*Journ. prakt. Chem.*, (1), **67**, 472, 1856) fuses the sulphide with lead oxide and ammonium nitrate. The excess in weight over the amount of PbO used represents the molybdic oxide—MoO₃; E. Döhler (*Chem. Ztg.*, **24**, 537, 1900) prefers gentle ignition of the sulphide in a Rose's crucible in a current of hydrogen and weighing as MoS₂; or ignition in a current of hydrogen at a higher temperature and weighing as metal, as recommended by O. F. von Pfordten (*Ber.*, **17**, 734, 1884); W. T. Taggart and E. F. Smith (*Journ. Amer. Chem. Soc.*, **18**, 1053, 1896) recommend igniting the sulphide with oxalic acid and weighing as MoO₃; and C. Friedheim and H. Euler (*Ber.*, **28**, 2061, 1895) ignite the sulphide at a high temperature in air and weigh as MoO₃.

[2] E. Collett and M. Eckardt, *Chem. Ztg.*, **33**, 968, 1909.

[3] Similar results were obtained by calcining ammonium molybdate, and fig. 102 applies to both this salt and to the sulphide.

[4] The sublimation of the oxide is shown by the presence of small glistening crystals above the mass in the crucible.

Determination of Molybdenum as Sulphide.—This determination is less liable to error and the result is rather more certain than by the preceding method, but the apparatus required is a little more complex. The washed sulphide precipitate is dried, the precipitate separated from the paper and preserved between two watch-glasses, while the filter-paper is burned to ash in a crucible. The sulphide is transferred to the same crucible, which is then fitted with a perforated lid (Rose's crucible, fig. 98, page 418), and the whole gently calcined to a constant weight in a current of hydrogen gas. The contents of the crucible are finally weighed as molybdenum sulphide—MoS_2. The equivalent weight of molybdenum trioxide is obtained by multiplying the weight of the sulphide by 0·8993.

For instance, working with a known amount of molybdenum trioxide, it was found that:

MoO_3 used	.	.	.	.	0·1413 0·1422 0·1500 grm.
MoS_2 found	.	.	.	.	0·1573 0·1578 0·1672 grm.
MoO_3 calculated from sulphide	.	0·1414 0·1419 0·1503 grm.

The results are therefore quite satisfactory.

§ 222. The Gravimetric Determination of Molybdenum as Lead Molybdate.

If a gravimetric process be required for the molybdenum in soluble salts like ammonium molybdate, dissolve, say, 0·5 grm. of the salt in 200 c.c. of water and add a few drops of ammonia, followed by 2 or 3 c.c. of (33 per cent.) acetic acid,[1] and 4 or 5 grms. of ammonium chloride. Heat the solution to boiling and while boiling add gradually, with constant stirring, 45–50 c.c. of a solution of lead acetate.[2] Boil two or three minutes more with vigorous agitation. The cream-coloured granular precipitate settles and filters rapidly. When the precipitate has settled, filter through an asbestos-packed Gooch crucible and wash by decantation with boiling water, containing 5 grms. of ammonium chloride or ammonium acetate and five drops of acetic acid per 200 c.c. Transfer all the precipitate to the Gooch crucible and, when the washings are free from lead, wash the precipitate twice with boiling water. Heat the crucible on an asbestos plate until dry and then over a naked flame. Cool in a desiccator and weigh as lead molybdate—$PbMoO_4$. Multiply the weight of the lead molybdate so obtained by 0·39213 to get the corresponding amount of MoO_3.

Errors.—If sulphates be present, as would be the case if the precipitated sulphide were dissolved in hot nitric acid, lead sulphate will be precipitated with the lead molybdate. Hence it is necessary to roast molybdenum sulphide to oxide before it is dissolved in acid, preparatory to precipitating as lead molybdate.

Cruser and Miller give the following trials with known amounts of molybdenum:

Used	.	.	0·14765 0·14793 0·17302 0·17211 0·19657 grm.
Found	.	.	0·14745 0·14793 0·17301 0·17210 0·19656 grm.

Vanadium, if present, interferes with the test. According to Brearley, the presence of acetic acid, lead acetate, alkali nitrates, chlorides and acetates, salts of manganese, copper, cobalt, nickel, zinc, magnesium, mercury, barium, strontium, calcium, arsenic, cadmium, phosphorus, aluminium and uranium

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[1] If more acetic acid be present, some lead molybdate may be dissolved.
[2] LEAD ACETATE SOLUTION.—Dissolve 4 grms. of the salt in 100 c.c. of water.

does not interfere; silicates give slightly high results; iron and chromium should be removed by the addition of sodium hydroxide to the boiling solution.[1]

§ 223. The Volumetric Determination of Molybdenum by Potassium, Permanganate.

Dissolve the sulphide in a beaker or dish by digestion with a mixture of 10 c.c. of concentrated sulphuric acid, 10 c.c. of hydrochloric acid and 5 c.c. of nitric acid. Evaporate [2] the solution until sulphurous fumes are evolved. Let the solution cool and then neutralise it with ammonia; add 10 c.c. of concentrated sulphuric acid and make the solution up to 200 c.c. When the solution has a temperature of 70°–75°, pour it through a reductor (page 173) with a column of granulated zinc [3] (20–30 mesh) about 37 or 38 cm. long. Arrange the suction so that it takes 6 minutes for the solution to pass through the reductor tube.[4] Titrate the solution immediately with standard potassium permanganate.[5] The test experiments are excellent.[6]

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[1] For some properties of lead molybdate, see page 341. A. de Wich (*Liebig's Ann.*, **83**, 222, 1861) precipitated the molybdenum as barium molybdate. T. M. Chatard, *Amer. J. Science*, (3), **1**, 416, 1871; *Chem. News*, **24**, 175, 1871; P. Guichard, *Compt. rend.*, **131**, 389, 419, 1900; H. Brearley, *Chem. News*, **78**, 203, 1898; **79**, 2, 14, 1899; F. Ibbotson and H. Brearley, *ib.*, **79**, 3, 1899; **81**, 269, 1900; *Analysis of Steel Works Materials*, London, 85, 273, 1902; L. Schindler, *Zeit. anal. Chem.*, **27**, 137, 1888; F. van Dyke Cruser and E. H. Miller, *Journ. Amer. Chem. Soc.*, **26**, 675, 1904; H. Westling and C. Anderson, *Min. Scient. Press*, **113**, 917, 1916; H. B. Weser, *Journ. Phys. Chem.*, **20**, 640, 1916; R. Strebinger, *Oester. Chem. Ztg.*, **20**, 226, 1917; J. Kassler, *Zeit. anal. Chem.*, **74**, 276, 1928; H. A. Doerner, *Metal Ind.*, **37**, 444, 1930; *Chem. Zentr.*, (1), 321, 1931; W. F. Murray, *Chemist-Analyst*, **18**, 10, 1929; W. Werz, *Zeit. anal. Chem.*, **80**, 109, 1930; L. A. Congdon and L. V. Rohner, *Chem. News*, **128**, 118, 1924; K. E. Stanfield, *Ind. Eng. Chem. Anal. Ed.*, **7**, 273, 1935. In mineral acid solution, α-benzoin oxime will separate molybdenum from all metals except tungsten, palladium, tantalum, chromates and vanadates—H. B. Knowles, *Bur. Standards Journ. Research*, **9**, 1, 1932; E. Taylor, *Analyst*, **62**, 107, 1937. For oxyquinoline as a precipitant, see W. Geilmann and F. Weibke, *Zeit. anorg. Chem.*, **199**, 347, 1931.

[2] The solution is inclined to bump badly. Blowing air through the solution during the evaporation prevents this.

[3] F. Pisani, *Compt. rend.*, **59**, 301, 1864; C. Rammelsberg, *Pogg. Ann.*, **127**, 281, 1866; A. Werneke, *Zeit. anal. Chem.*, **14**, 1, 1875; H. Bornträger, *Zeit. anal. Chem.*, **37**, 438, 1898; W. Scott, *Journ. Ind. Eng. Chem.*, **12**, 578, 1920; T. Nakazono, *Journ. Chem. Soc. Japan*, **42**, 526, 1921; K. Someya, *Zeit. anorg. Chem.*, **145**, 168, 1925; E. Müller, *Elektrochem. Zeit.*, **33**, 182, 1927; Th. Döring, *Zeit. anal. Chem.*, **82**, 193, 1930; B. Stehlik, *Coll. Czech. Chem. Comm.*, **4**, 418, 1932; *Chem. Listy*, **26**, 533, 1932; J. Kassler, *Zeit. anal. Chem.*, **75**, 457, 1928.

[4] There has been some discussion on the product obtained by reducing molybdic salts. Some say that Mo_2O_3 is formed (W. A. Noyes and E. D. Frohman, *Journ. Amer. Chem. Soc.*, **16**, 553, 1894); others consider that $Mo_{24}O_{37}$ is obtained (A. A. Blair and J. E. Whitfield, *Journ. Amer. Chem. Soc.*, **17**, 747, 1895); others, again, say that the reduction does not go so far as this. E. H. Miller and H. Frank (*ib.*, **25**, 919, 1903) did not get Mo_2O_3 in the reductor, but they could find no definite stopping-place at $Mo_{24}O_{37}$, although reduction under the usual conditions proceeds very close to this. With the reductor arranged as described in the text, the iron standard of the permanganate multiplied by 0·88 gives the equivalent MoO_3 standard, and by 0·01579, the phosphorus standard. With amalgamated zinc, the factors were 0·8842 and 0·01586 respectively. If the reduction had been to $Mo_{24}O_{37}$, the factors would have been 0·8832 and 0·01584 respectively. It is best to standardise the potassium permanganate by the method of reduction with known solutions of molybdate. See page 677.

[5] STANDARD SOLUTION OF AMMONIUM MOLYBDATE.—Dissolve 6·132 grms. of ammonium molybdate—$(NH_4)_6Mo_7O_{24}.4H_2O$—in a litre of water. The solution contains the equivalent of 0·005 grm. MoO_3 per c.c. The strength of the solution may be verified by precipitation of the molybdenum as lead molybdate—page 450. The potassium permanganate solution is approximately 0·1N, and it is standardised by running the standard ammonium molybdate solution through the reductor and titrating as described in the text.

[6] For the volumetric determination of molybdenum by *methylene blue*, see E. Knecht and F. W. Atack, *Analyst*, **36**, 98, 1911; by *potassium iodate*, G. S. Jamieson, *Journ. Amer. Chem. Soc.*, **39**, 246, 1917; by *titanous chloride*, A. Travers, *Compt. rend.*, **165**, 362, 1917; H. H. Willard and F. Fenwick, *Journ. Amer. Chem. Soc.*, **45**, 928, 1923; by *chromous chloride*,

§ 224. The Separation of Tungsten and Molybdenum— (a) Hommel's Process.

The analogies in the properties of tungsten and molybdenum [1] compounds render a separation of the two elements difficult.[2]

Tungsten and molybdenum can be separated by the action of warm sulphuric acid (sp. gr. 1·378) upon the moist freshly precipitated [3] oxides MoO_3 and WO_3.[4] The former passes into solution, the latter remains insoluble. Hommel says that this process only gives satisfactory results when the moist oxides are first digested with concentrated sulphuric acid and a few drops of dilute nitric acid, say, in a porcelain dish over a naked flame for about half an hour.[5] When the solution is cold, add about three times its volume of water. Filter, wash the precipitate with dilute sulphuric acid (1 : 20), and finally wash it two or three times with alcohol, ignite as indicated on page 441, and weigh as WO_3. The molybdenum in the filtrate may be precipitated by hydrogen sulphide (page 446), or, if only small quantities are present, the solution may be evaporated to dryness and the residue weighed in a platinum dish. Hommel's process is quite satisfactory. For example, Hommel obtained the following results with artificial mixtures of tungsten and molybdenum trioxides :

Table LI.—Test Analyses, Tungsten and Molybdenum Mixtures.

Tungstic trioxide.		Molybdenum trioxide.	
Used.	Found.	Used.	Found.
0·9616	0·9614	0·1077	0·1080
0·8732	0·8738	0·0501	0·0503
0·7029	0·7035	0·1030	0·1028
0·5737	0·5740	0·1184	0·1180

H. Brintzinger and F. Oschatz, *Zeit. anorg. Chem.*, **165**, 221, 1927; H. Brintzinger and W. Schieferdecker, *Zeit. anal. Chem.*, **78**, 110, 1929; by *lead acetate*, E. Rother and G. Jander, *Zeit. angew. Chem.*, **43**, 930, 1930; T. Raïkhinshtein and N. Korobov, *Journ. Gen. Chem.* (*U.S.S.R.*), **2**, 661,1932; by *ceric sulphate*, N. H. Furman and W. M. Murray, junr., *Journ. Amer. Chem. Soc.*, **58**, 1689, 1843, 1936. For colorimetric methods, see W. J. King, *Ind. Eng. Chem.*, **15**, 350, 1923; O. L. Magg and C. H. McCollam, *ib.*, **17**, 524, 1925; H. ter Meulen, *Chem. Weekb.*, **22**, 80, 1925; E. Wendehorst, *Zeit. anorg. Chem.*, **144**, 319, 1925; A. D. Funck, *Zeit. anal. Chem.*, **68**, 283, 1926; J. Kassler, *Chem. Ztg.*, **51**, 953, 1927; T. R. Cunningham and H. L. Hamer, *Ind. Eng. Chem. Anal. Ed.*, **3**, 106, 1931; L. H. James, *ib.*, **4**, 89, 1932; L. C. Hurd and F. Reynolds, *ib.*, **6**, 477, 1934; K. E. Stanfield, *ib.*, **7**, 273, 1935; E. B. Sandell, *ib.*, **8**, 336, 1936; K. Agte, H. Becker-Rose and G. Heyne, *Zeit. angew. Chem.*, **38**, 1121, 1925; G. A. Patchenko, *Journ. App. Chem.* (*U.S.S.R.*), **8**, 722, 1935. For the electro-analysis of molybdenum, see C. Nemoto and Y. Tanabe, *Journ. Electrochem. Assoc.* (Japan), **2**, 53, 1934.

[1] Commercial tungstic acid may contain molybdenum — E. Corleis, *Liebig's Ann.*, **232**, 265, 1886; A. G. Krüss, *ib.*, **225**, 29, 1884; H. Traube, *Neues Jahrb. Min.*, B.B., **7**, 232, 1891; C. Friedheim and R. Meyer, *Zeit. anorg. Chem.*, **1**, 76, 1892.

[2] E. F. Smith and R. H. Bradbury, *Ber.*, **24**, 2930, 1891; E. E. Marbaker, *The Separation of Tungsten from Molybdenum*, Penn., 1914; *Journ. Amer. Chem. Soc.*, **37**, 86, 1915.

[3] If the oxides have been ignited, it is best to fuse them with from four to six times their weight of sodium carbonate, dissolve the fused mass in water, evaporate the solution to dryness and add the concentrated sulphuric and nitric acid as described in the text.

[4] E. D. Desi, *Journ. Amer. Chem. Soc.*, **19**, 213, 1897; M. J. Ruegenberg and E. F. Smith, *ib.*, **22**, 772, 1900; *Chem. News*, **83**, 5, 1901; W. Hommel, *Ueber die quantitative Trennung von Wolfram und Molybdän*, Zürich, 1902.

[5] If the solution is greenish coloured, add a drop or two more of dilute nitric acid to oxidise the tungstic oxide to yellow tungstic acid.

(b) Rose's Tartaric Acid Process.

In Rose's method,[1] the alkali salts under investigation are treated with an excess of sulphuric acid, and the tungsten is kept in solution by the addition of a considerable amount of tartaric acid [2] while the molybdenum is precipitated by hydrogen sulphide in a pressure flask. The tartaric acid is afterwards destroyed by repeated evaporation with nitric acid (page 195), and the tungsten finally separated in the usual manner as WO_3. Friedheim and Meyer [3] have raised the question: Is all the molybdenum precipitated in the presence of the tartaric acid? The trial results with known mixtures of molybdenum and tungsten are, however, satisfactory. The objection to the process rests on the time consumed in the destruction of the large quantities of tartaric acid.[4]

§ 225. The Separation of Tungsten and Molybdenum—Péchard's Process.

Debray [5] found that a very volatile crystalline compound, $MoO_3.2HCl$, is formed when molybdic acid is exposed to the action of hydrogen chloride. The reaction is represented by—

$$Na_2MoO_4 + 4HCl = 2NaCl + H_2O + MoO_3.2HCl$$

and Péchard [6] found that the reaction can be used for separating molybdenum from tungsten. Thus, if a weighed mixture of tungsten and molybdenum (oxides or alkali salts) be placed in a boat and heated between 250° and 270° in a current of dry hydrogen chloride, the molybdenum is volatilised as $MoO_3.2HCl$ and deposited in the form of long acicular white crystals in the cooler parts of the tube, while tungsten oxide remains behind in the boat.

The Apparatus.—The arrangement indicated in fig. 103 may be used for the purpose. A piece of wide glass tubing D holds a boat containing a weighed quantity of the mixed oxides. The tube is connected at one end with an apparatus for generating hydrogen chloride. The hydrogen chloride gas is passed through a wash-bottle A, containing concentrated hydrochloric acid, and dried by passing through a wash-bottle B containing concentrated sulphuric acid. The opposite end of the tube is connected with an absorption tube E containing a little water.

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[1] H. Rose, *Handbuch der analytischen Chemie*, Braunschweig, 2, 358, 1871.

[2] J. Lefort, *Ann. Chim. Phys.*, (5), 9, 93, 1877; I. Koppel (*Chem. Ztg.*, 48, 801, 1924) neutralises an alkaline solution of molybdate and tungstate with formic acid, treats the solution with a small quantity of ammonium sulphide and then acidifies with formic acid. On warming, molybdenum sulphide alone is precipitated. Compare H. Yagoda and H. A. Fales, *Journ. Amer. Chem. Soc.*, 58, 1494, 1936.

[3] C. Friedheim and R. Meyer, *Zeit. anorg. Chem.*, 1, 76, 1892.

[4] See H. B. Merrill (*Journ. Amer. Chem. Soc.*, 43, 2383, 1921) for the separation of molybdenum and tungsten by selenium oxychloride; D. Hall (*Journ. Amer. Chem. Soc.*, 44, 1462, 1922) for the determination of small amounts of molybdenum in tungsten by xanthic acid.

[5] H. Debray, *Compt. rend.*, 46, 1098, 1858; *Liebig's Ann.*, 108, 250, 1858; *Journ. prakt. Chem.*, (1), 76, 160, 1859.

[6] E. Péchard, *Compt. rend.*, 114, 173, 1891; *Zeit. anorg. Chem.*, 1, 262, 1892; *Chem. News*, 65, 89, 1892; E. F. Smith and U. Oberholtzer, *Journ. Amer. Chem. Soc.*, 15, 18, 1893; *Chem. News*, 67, 6, 1893; *Zeit. anorg. Chem.*, 4, 237, 1893; E. F. Smith and P. Maas, *ib.*, 5, 280, 1894; *Chem. News*, 67, 207, 1893; *Journ. Amer. Chem. Soc.*, 15, 397, 1893; *Journ. Franklin Inst.*, 136, 443, 1893; L. Moser and K. Schmidt (*Monats.*, 47, 313, 1926) use carbon tetrachloride and air.

The Sublimation.—The tube containing the boat is heated to 270° [1] in the tube oven *C*, fitted with thermometer and thermostat. The sublimate of $MoO_3.2HCl$ is driven forward into the absorption tube, every now and again, by heating the fore part of the combustion tube *D* with a naked Bunsen flame.

The Tungstic Oxide.—When sublimation has ceased (about 1½ hours), the boat may contain tungsten oxide with or without sodium chloride, according to the nature of the substance under investigation. The sodium chloride, if present, is removed by washing the residue with water; the tungsten oxide is
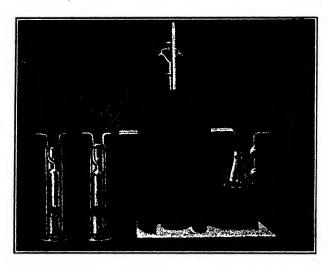
Fig. 103.—Separation of Molybdenum from Tungsten.

filtered into a weighed Gooch crucible, ignited as indicated on page 92 and weighed as tungsten trioxide—WO_3.

The Molybdic Oxide.—The molybdic hydrochloride decomposes in contact with the water, forming a brick-red chloride—$Mo_3O_5Cl_8$—insoluble in hydrochloric acid, but readily soluble in nitric acid. The sublimate is washed from the combustion tube and from the absorption tube into an evaporating basin with water containing a little nitric acid. The solution is evaporated to dryness on a water bath; the residue is dissolved in a little ammonia, evaporated to dryness, ignited as indicated on page 448 and weighed as molybdenum trioxide—MoO_3.

The Results.—The separations by this process are excellent. For instance, with artificial mixtures:

Tungstic oxide used .	0·2834 grm.	Molybdic oxide used .	0·0386 grm.
Tungstic oxide found .	0·2838 grm.	Molybdic oxide found .	0·0380 grm.

The comparatively elaborate apparatus is considered a disadvantage in the laboratory of a works. This objection would not be serious if a large number of determinations had to be made. The time factor is then significant.[2]

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[1] If the temperature be much greater than 270°, tungsten may sublime; if much less, the separation may be incomplete.

[2] For the separation of tungsten and vanadium, see C. Friedheim, *Ber.*, **23**, 352, 1890; *Chem. News*, **65**, 27, 1892; A. Rosenheim and C. Friedheim, *Zeit. anorg. Chem.*, **1**, 313, 1892; C. Friedheim, W. H. Henderson and A. Pinagel, *ib.*, **45**, 396, 1905; C. Friedheim and

§ 226. The Determination of Columbium and Tantalum.

The elements columbium and tantalum are often associated with tungsten, and, if present, they will be precipitated with the tungsten trioxide. Many tantalum minerals are, however, free from tungsten. Since tantalum is now one of the "industrial elements," the analysis of compounds containing tantalum, especially ferrous alloys,[1] is sometimes required.

The exact determination and separation of columbium and tantalum has long been one of the unsolved problems in analytical chemistry. However, since 1921 a series of papers by Schoeller and co-workers has cleared up the main difficulties encountered by their predecessors and has enabled a definite position to be given to these two elements in the analytical scheme. In the earlier process of Simpson[2] the mineral is opened up by fusion with potassium hydroxide; the cold melt is dissolved in excess of hydrochloric acid and columbium and tantalum pentoxides are precipitated by hydrolysis, together with tungsten, silica, tin and antimony, if present. After removal of the tungstic oxide by ammonia[3] and the silica by hydrofluoric and sulphuric acids, the ignited residue is reduced in hydrogen and the metallic tin and antimony dissolved away in hydrochloric acid, leaving only the mixed pentoxides of columbium and tantalum. The chief weakness of the process is that columbium and tantalum are not completely precipitated by hydrolysis, particularly if much titanium be present.

Marignac's classical process[4] for the separation of tantalum and columbium is based upon the different solubilities of potassium heptafluotantalate—K_2TaF_7—and of potassium oxypentafluocolumbate—$K_2CbOF_5.H_2O$.[5] One part of the latter salt is soluble in 12-13 parts of cold water, while 1 part of potassium fluotantalate dissolves in 150-157 parts of cold water. The degree of accuracy is said to be to about 1 per cent. or even as high as 0·5 per cent., if 20 to 25 grms. of the mineral be taken for analysis.[6]

C. Castendyck, *Ber.*, 33, 611, 1900; W. Gibbs, *Zeit. anal. Chem.*, 23, 543. 1884; 25, 544, 1886; *Amer. Chem. Journ.*, 4, 377, 1882; 5, 378, 1883; 1, 219, 1879; F. Mohr, *Lehrbuch der chemischen-analytischen Titriermethode*, Braunschweig, 314, 1877; A. Šafařik, *Liebig's Ann.*, 109, 84, 1859; C. R. von Hauer, *Ber. Wien. Akad.*, 39, 448, 1860; A. Rosenheim, *Ber.*, 23, 3208, 1890; P. E. Browning and R. J. Goodman, *Zeit. anorg. Chem.*, 13, 427, 1897; C. Reichard, *Chem. Ztg.*, 27, 4, 1903; F. Rothenbach, *Ber.*, 23, 3050, 1890; A. Carnot, *Compt. rend.*, 104, 1803, 1850, 1887; 105, 119, 1887; A. Jilek and J. Lukas, *Coll. Czech. Chem. Comm.*, 1, 263, 1929; *Chem. Listy*, 24, 73, 1930; G. Fenner, *Chem. Ztg.*, 42, 403, 1918.

[1] G. L. Kelley, F. B. Myers and C. B. Illingworth, *Journ. Ind. Eng. Chem.*, 9, 852, 1917; L. Silverman, *ib.*, *Anal. Ed.*, 6, 287, 1934; A. Travers, *Compt. rend.*, 166, 494, 1918; K. Swoboda and R. Horny, *Zeit. anal. Chem.*, 80, 271, 1930.

[2] E. S. Simpson, *Bull. West Australia Geol. Sur.*, 23, 72, 1906; *Chem. News*, 99, 243, 1909. Compare J. Moir, *Journ. Chem. Met. Min. Soc. S. Africa*, 16, 189, 1916; W. Stahl, *Chem. Ztg.*, 56, 175, 1932.

[3] J. A. Tschernichov and M. P. Karsajevskaya (*Zeit. anal. Chem.*, 98, 97, 1934) state that this procedure is not satisfactory.

[4] C. de Marignac, *Ann. Chim. Phys.*, (4), 8, 5, 49, 1865; E. S. Simpson, *Bull. West Australia Geol. Sur.*, 23, 71, 1906; A. Tighe, *Journ. Soc. Chem. Ind.*, 25, 681, 1907; O. Ruff and E. Schiller, *Zeit. anorg. Chem.*, 72, 329, 1911; E. Meimberg, *Zeit. angew. Chem.*, 26, 83, 1913; E. Meimberg and P. Winzer, *ib.*, 26, 157, 1913; C. Wenzel, *Anal. Asoc. Quim. Argentina*, (2), 297, 1923. For other methods proposed for the separation of columbium and tantalum, see H. B. Merrill, *Journ. Amer. Chem. Soc.*, 43, 2378, 1921; G. W. Sears, *ib.*, 48, 343, 1926; 51, 122, 1929; D. D. Peirce, *ib.*, 53, 2810, 1931; H. Pied, *Compt. rend.*, 179, 897, 1924; O. Ruff and F. Thomas, *Zeit. anorg. Chem.*, 156, 213, 1926; V. Scharz, *Angew. Chem.*, 47, 228, 1934.

[5] Or $2KF.CbOF_3.H_2O$. G. Krüss and L. F. Nilson, *Ber.*, 20, 1676, 1887.

[6] O. Hauser and A. Lewite, *Zeit. angew. Chem.*, 25, 100, 1912.

§ 227. Schoeller's Process.

The following is an attempt to combine the subject-matter of the numerous papers of Schoeller and co-workers so as to give in the most general case the main outlines of a scheme for the analysis of a mineral containing columbium and tantalum.

Opening-up.[1]—Fuse 0·5 grm. of the very finely powdered substance with about 4 grms. of silica-free potassium bisulphate in a silica crucible until all is in a quiet state of fusion. Rotate the crucible so as to spread the melt over its sides and then cool. Add about 40 c.c. of a hot 10 per cent. solution of tartaric acid to the contents of the crucible and stand for some time. Transfer the loosened mass to a 400 c.c. beaker and thoroughly rinse the crucible with hot water.

Removal of Silica.[2]—The extract and washings, from the above, which should occupy about 100 c.c., are *stirred continuously* until the cake has disintegrated, after which the liquid is heated to incipient boiling, but at no time during this procedure should the precipitate be allowed to settle. The silica which separates is filtered off, washed, ignited and weighed as usual. After treatment with hydrofluoric and sulphuric acids, the silica residue,[3] if any, is fused with a fragment of potassium bisulphate. The melt is extracted, as previously, with a little tartaric acid solution and the solution from the cake added to the filtrate from the silica.

Removal of Tin, Antimony, etc.— The combined solutions are treated with 5 c.c. of 10 per cent. sulphuric acid, heated to 70°-80° and saturated with hydrogen sulphide until cold. After standing the beaker for some hours in a warm place, the precipitate is filtered off and washed with acidulated hydrogen sulphide water.[4]

Precipitation of Columbic and Tantalic Acids—Major Fraction.[5] The filtrate from the hydrogen sulphide precipitation is treated with 30 to 35 c.c. of concentrated hydrochloric acid and boiled for a few minutes, when the bulk of the columbic and tantalic acids is precipitated, together with variable amounts of tungstic acid,[6] zirconium and titanium, if these are present. Some filter-paper pulp is added and the precipitate is left to settle, after which it is filtered off, washed with 2 per cent. hydrochloric acid and ignited in a weighed silica crucible.

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[1] W. R. Schoeller, *Analyst*, **56**, 304, 1931. For reviews of analytical methods, see W. R. Schoeller, *Analyst*, **61**, 806, 1936; *The Analytical Chemistry of Tantalum and Niobium*, London, 1937; L. Bleyenheuft, *Ing. Chim.*, **20**, 165, 1936.

[2] W. R. Schoeller and A. R. Powell, *Analyst*, **53**, 258, 1928; W. R. Schoeller, *ib.*, **59**, 667, 1934.

[3] The residue may contain lead and barium sulphates and also tin oxide. For the separation of tin from columbium, tantalum and silica, see W. R. Schoeller and H. W. Webb, *Analyst*, **56**, 800, 1931.

[4] The sulphide precipitate may contain a little columbic and tantalic acids. These are recovered by dissolving the precipitate in 8 c.c. of sulphuric acid and enough nitric acid to destroy the organic matter. After fuming off the excess of nitric acid, cool, add 10 c.c. of 20 per cent. tartaric acid, 25 c.c. of warm water and a moderate excess of ammonia. Pour the mixture into a freshly prepared solution of yellow ammonium sulphide to precipitate copper and bismuth sulphides. Filter and acidify the filtrate with acetic acid to precipitate antimony sulphide—E. F. Waterhouse and W. R. Schoeller, *Analyst*, **57**, 284, 1932.

[5] W. R. Schoeller and H. W. Webb, *Analyst*, **54**, 704, 1929.

[6] Note that the balance of the tungstic acid is not all brought down in the subsequent tannin precipitation—W. R. Schoeller and C. Jahn, *Analyst*, **59**, 465, 1934. Compare W. R. Schoeller and E. F. Waterhouse, *Analyst*, **61**, 449, 1936.

Removal of Iron and Manganese.[1]—The filtrate and washings from the previous operation are evaporated down to about 20 c.c. After reduction of the iron to the ferrous state by hydrogen sulphide, a good excess of concentrated ammonia and about 10 c.c. of freshly prepared ammonium sulphide solution are added. The whole of the iron and all but a few mgrms. of the manganese are precipitated. The precipitate is allowed to settle in a warm place for some hours, then filtered off and washed with warm water containing a little ammonium chloride and sulphide.[2]

Recovery of the Balance of the Columbic and Tantalic Acids.[3]—The filtrate and washings from the iron and manganese precipitation are slightly acidified with acetic acid and boiled until all the hydrogen sulphide has been expelled. A concentrated, freshly prepared solution of 1 grm. of tannin in water is added to the boiling solution. The balance of the columbic and tantalic acids, titanium and zirconium are precipitated, together with any aluminium which may be present [4] and some but not all of the balance of the tungstic acid. The precipitate is coagulated by standing on a water bath, filtered off and washed [5] with a 2 per cent. solution of ammonium chloride, containing 0·05 per cent. of tannin. It is then ignited in the crucible, containing the major fraction of the columbic and tantalic acids, and weighed.

In the most general case the precipitate contains tantalum, columbium, titanium, zirconium, hafnium, aluminium, tungsten, uranium, thorium and rare earths.

Separation of Columbium, Tantalum and Titanium.[6]—The precipitate is fused up with sodium bisulphate and the cold melt is dissolved in a saturated solution of ammonium oxalate (3 grms.). The boiling solution is gradually neutralised with 1·0N-ammonia solution until a faint opalescence appears, which is then cleared up by adding the minimum amount of 1·0N-hydrochloric acid. After adding an equal volume of saturated ammonium chloride solution, the boiling is continued and a 5 per cent. solution of tannin is added drop by drop from a burette. Stand on a hot plate until the solution clears. Filter, wash with a 5 per cent. solution of ammonium chloride, containing 1 per cent. of ammonium oxalate, and ignite.

The precipitate is again fused up with sodium bisulphate, the whole process of extraction and precipitation being repeated exactly as above. The final precipitate should now consist solely of columbium, tantalum and titanium oxides.[7]

Separation of Titanium from Columbium and Tantalum.—For full details see Section 280, page 565. Where a subsequent separation of columbium and

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[1] W. R. Schoeller, *Analyst*, 59, 667, 1934. Uranium is not precipitated by ammonium sulphide in ammoniacal tartrate solution—W. R. Schoeller and H. W. Webb, *Analyst*, 58, 143, 1933.

[2] The iron and manganese are subsequently separated by the basic acetate process (see page 383). The iron is determined as oxide and the manganese as phosphate.

[3] W. R. Schoeller and H. W. Webb, *Analyst*. 54, 704, 1929; W. R. Schoeller, *ib.*, 56, 304, 1931; 59, 667, 1934.

[4] Thorium and the rare earths, if present, will also be precipitated; as will some phosphorus and vanadium, if present—W. R. Schoeller and H. W. Webb, *Analyst*, 61, 585, 1936.

[5] For details of filtering and washing, see W. R. Schoeller, *Analyst*, 56, 308, 1931.

[6] W. R. Schoeller and A. R. Powell, *Analyst*, 57, 550, 1932.

[7] Assuming that tungsten is absent; if present the precipitate will probably contain more or less tungstic oxide. In this case the mixed oxides are fused with potassium carbonate and the aqueous extract of the melt is treated with a slightly ammoniacal magnesium salt solution, when the earths are precipitated, while alkali tungstate remains in solution. A double precipitation should be made—A. R. Powell, W. R. Schoeller and C. Jahn, *Analyst*, 60, 506, 1935.

tantalum is not necessary, the titania can be determined colorimetrically, and its weight deducted from the weight of mixed oxides.

Separation of Columbium and Tantalum.[1]—This separation is based on the facts that whereas both columbium and tantalum are precipitated by tannin from their ammoniacal oxalate solutions, only tantalum is precipitated in slightly acid solution. However, when both are present some columbium will be co-precipitated with the tantalum.

As the tantalum-tannin complex is yellow and that given by columbium is red, the presence of the latter is shown by the orange colour of the tannin precipitate.

Since co-precipitation is unavoidable, fractional precipitation must be applied and the method seeks to produce (1) a columbium-free tantalum fraction, (2) a mixed columbium-tantalum fraction, and (3) a columbium filtrate free from tantalum. The middle fraction is refractionated into three similar fractions and the middle one of these again fractionated. All the pure yellow tantalum precipitates are ignited together and all the filtrates are combined and the columbium in them precipitated by tannin in ammoniacal solution. For full experimental details, the original paper should be consulted.[2]

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[1] W. R. Schoeller, *Analyst*, 57, 750, 1932.

[2] W. R. Schoeller and C. Jahn (*Analyst*, 51, 619, 1926) have described a volumetric process for the simultaneous determination of columbium and tantalum, which gives approximate results. Compare A. R. Powell, W. R. Schoeller and C. Jahn, *Analyst*, 60, 513, 1935. For a colorimetric method for columbium and tantalum, see N. F. Krivoshlykov and M. S. Platonov, *Journ. App. Chem. (U.S.S.R.)*, 10, 184, 191, 1937.

CHAPTER XXXI.

DETERMINATION OF GOLD, PLATINUM AND SELENIUM.

§ 228. The Detection of Gold.

IN the normal schemes of qualitative analysis gold is precipitated with those metals whose sulphides are insoluble in acid solution; in cold solution a brownish-black sulphide is precipitated, while brown metallic gold is precipitated from hot solutions. Gold solutions are reduced by many reagents, e.g. ferrous sulphate and stannous chloride, giving colloidal solutions of gold with a marked coloration.

Tests for Gold. —(1) *Pozzi-Escot's Test.*[1]—The solution is acidified, if necessary, with formic acid and a few drops of a solution of phenylhydrazine hydrochloride are added. The least trace of gold is shown by the production of a bluish-violet colour by transmitted light.

(2) *Malatesta and Nola's Test.*[2]— Traces of gold give an intense blue colour, changing to purple, when the solution is treated with a solution of benzidine.[3] In the presence of free acetic acid the colour is green, which changes to blue on adding excess of the reagent. One part of gold can be detected in 300,000 parts of solution. Platinum salts [4] after 10 minutes give a blue flocculent precipitate, sensitive to 1 in 80,000; iron also gives a blue colour which is stable only in the presence of excess of benzidine.

(3) *Pollard's Test.*[5]—One part of gold in a million of water can be detected by the bright yellow colour given on adding 1 c.c. of a solution of ortho-tolidine,[6] and in a solution containing one part of gold in 20 millions of water the yellow colour can just be detected in a depth of 10 cms. of liquid. Ruthenium, iron, osmic acid and vanadates also give yellow colours, but no other metals. In the presence of copper the colour is green. As the test is also given by chlorine, it is essential that free chlorine should be absent. Reducing agents, especially nitrous acid, vitiate the test, and large amounts of strong mineral acids should be absent.[7]

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[1] M. E. Pozzi-Escot, *Ann. Chim. anal.*, **12**, 90, 1907.

[2] G. Malatesta and E. di Nola, *Boll. Chim. farm.*, **52**, 461, 1913; N. A. Tananev and K. A. Dolgov, *Journ. Russ. Phys. Chem. Soc.*, **61**, 1377, 1929.

[3] BENZIDINE REAGENT.—Dissolve 1 grm. of benzidine in 10 c.c. of glacial acetic acid and 50 c.c. of water.

[4] For the reactions of the platinum metals with benzidine, see S. C. Ogburn, junr., *Journ. Amer. Chem. Soc.*, **48**, 2499, 1926; V. G. Chlopin, *Ann. Inst. Platine*, **4**, 324, 1926.

[5] W. B. Pollard, *Analyst*, **44**, 94, 1919; *Bull. Inst. Min. Met.*, No. 223, 1923.

[6] ORTHO-TOLIDINE REAGENT.—Dissolve 1 grm. of o-tolidine in a litre of 10 per cent. hydrochloric acid.

[7] For other colour reactions of gold, see J. E. Saul, *Analyst*, **38**, 54, 1913; H. I. Cole, *Phillipine Journ. Sci.*, **21**, 361, 1922; P. Sporcq, *Bull. Soc. chim. Belg.*, **38**, 21, 1929; H. Holzer, *Mikrochem.*, **8**, 271, 1930; H. Holzer and W. Reif, *Zeit. anal. Chem.*, **92**, 12, 1933; K. Bihlmaier, *Mitt. Forsch. Inst. Probier. Edelmetalle*, **8**, 85, 1934.

§ 229. The Detection of the Platinum Metals.

Like gold, all the platinum metals are precipitated by hydrogen sulphide from solutions containing 2·5 to 3 per cent. by volume of free hydrochloric acid, except iridium, which needs an acid concentration of 20 per cent. by volume for complete precipitation. From a solution of all six metals, osmium and ruthenium are conveniently removed as their volatile tetroxides by distillation in a current of chlorine.[1] See page 476.

Tests for Palladium. ·(1) Palladium alone of the platinum metals is precipitated in *cold* hydrochloric acid solution by a 1 per cent. alcoholic solution of dimethylglyoxime.[2] The precipitate is yellow.

(2) *Feigl and Krumholz's Test.*[3]—1 c.c. of a faintly acid solution is boiled with 5 drops of a 5 per cent. solution of phosphomolybdic acid and treated with a rapid current of carbon monoxide. A blue or green colour is produced within a few minutes, depending on the amount of palladium present. The reaction is said to detect 1 part of palladium in 40,000,000 of solution. The other platinum metals do not interfere; gold, mercury and ferric iron diminish the sensitivity. Arsenic acid in concentrated solution and also arsenious acid give a blue colour. Strong oxidising and reducing agents should be absent.

Test for Platinum.—In hydrochloric acid solution platinum salts give with stannous chloride a colour which varies from yellow, through orange, to red, according to the amount of platinum present.[4] On standing, or more rapidly on warming, the colour darkens and the solution may finally become black. Organic matter must be absent, as it gives a similar coloration with stannous chloride. The presence of oxidising agents is for obvious reasons inadmissible.

Tests for Rhodium.—The platinum complex formed in the above test is soluble in ethyl acetate. Hence by shaking the solution twice with twice its volume of ethyl acetate the platinum can be extracted. Rhodium can be detected in the aqueous solution (1) by boiling, when a brown colloidal solution of the metal is obtained which develops a fine crimson colour on standing,[5] or (2) by the red colour given on the addition of alkali iodide.[6] This latter coloured complex is likewise soluble in ethyl acetate so that, after standing for 1 to 2 hours for the colour to develop, extraction with ethyl acetate removes the rhodium.

Tests for Iridium.—(1) If the aqueous solution above, left after extraction of the rhodium, be treated with chlorine water, a brown colour is formed if iridium is present.[7]

(2) Tetravalent iridium in 0·001 per cent. solution gives a sky-blue colour with benzidine.[8]

[1] For schemes for the detection and qualitative separation of the platinum metals, see H. Wölbling, *Ber.*, 67B, 773, 1934; S. C. Ogburn, junr., *Journ. Amer. Chem. Soc.*, 48, 2507, 1926; S. O. Thompson, F. E. Beamish and M. Scott, *Ind. Eng. Chem. Anal. Ed.*, 9, 420, 1937.

[2] M. Wunder and V. Thuringer, *Ann. Chim. anal.*, 17, 201, 1912; S. C. Ogburn, *l.c.*, 48, 2508, 1926; P. C. Putnam, E. J. Roberts and D. H. Selchow, *Amer. Journ. Sci.*, (5), 15, 423, 1928; H. Wölbling, *Ber.*, 67B, 773, 1934.

[3] F. Feigl and P. Krumholz, *Ber.*, 63B, 1917, 1930. For the detection of palladium by derivatives of 8-hydroxyquinoline, see G. Gutzeit and R. Monnier, *Helv. Chim. Acta*, 16, 223, 1933.

[4] L. Wöhler, *Verh. deut. Naturforsch. Aerzte*, (2), 105, 1907; E. Langstein and P. H. Prausnitz, *Chem. Ztg.*, 38, 802, 1914; S. C. Ogburn, *l.c.*, 48, 2497, 1926; H. Wölbling, *Ber.*, 67B, 773, 1934.

[5] V. N. Ivanov, *Journ. Russ. Phys. Chem. Soc.*, 49, 601, 1917; 50, 460, 1918.

[6] H. Wölbling, *l.c.*　　　　　　　　[7] H. Wölbling, *l.c.*

[8] V. G. Chlopin, *Ann. Inst. Platine*, 4, 324, 1926.

(3) The solution is evaporated to dryness and the residue heated with a slight excess of concentrated sulphuric acid to expel chlorine. After cooling slightly, ammonium nitrate is added in successive small quantities; the heating is continued and more ammonium nitrate added, when a deep blue colour is formed, if only 0·001 mgrm. of iridium is present. Gold, platinum, rhodium and ruthenium do not interfere, but in the presence of the first metal the colour is green.[1]

Test for Osmium. Tschugaev's Test.[2]—Osmium as osmic acid or osmichloride, when warmed for a few minutes with an excess of thiourea and a few drops of hydrochloric acid, gives a deep red to rose-coloured solution. As the test fails in the presence of nitric acid, which destroys the thiourea, an excess of sulphurous acid should be added, followed by a few crystals of thiourea, and the solution warmed on a water bath. The test will detect one part of osmium in a million.[3]

Tests for Ruthenium. (1) *Wöhler and Metz's Test.*[4]—When a solution containing ruthenium is heated for a short time with thiocarbanilide and hydrochloric acid, a blue colour is produced which can be extracted with ether. The test is sensitive to 0·003 mgrm. of ruthenium per c.c. Under similar conditions osmium gives a red complex soluble in ether.

(2) *Wölbling and Steiger's Test.*[5]—A 0·2 per cent. solution of rubianic acid, $(NH_2CS)_2$, in glacial acetic acid gives a strictly specific blue coloration with neutral or slightly acid solutions of ruthenium salts. The colour develops slowly in the cold, but rapidly at 100°. The reaction will detect 0·0002 mgrm. of ruthenium.

§ 230. The Precipitation of Gold and Platinum.

As stated already, gold is precipitated from cold acid solutions by hydrogen sulphide as a dark brown sulphide [6]; if the solution be hot, some metallic gold is also precipitated. The sulphide dissolves in alkali monosulphide extremely slowly, but a little more quickly in the polysulphide and forms a brownish-red solution.[7] If, therefore, the attempt be made to separate gold from the precipitate of mixed sulphides by ammonium or sodium monosulphide, part of the gold will be found with the tin, antimony and arsenic; and part with the metals insoluble in alkali sulphide.[8]

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[1] L. de Boisbaudran, *Compt. rend.*, **96**, 1336, 1883; P. E. Browning, *Introduction to the Rarer Elements*, New York, 177, 1908; V. N. Ivanov, *Journ. Russ. Phys. Chem. Soc.*, **44**, 1772, 1912; *Chem. Ztg.*, **37**, 157, 1913; *Chem. Zentr.*, (1), 844, 1913.

[2] L. Tschugaev, *Compt. rend.*, **167**, 235, 1918; R. Gilchrist, *Bur. Standards Journ. Research*, **6**, 421, 1931; S. C. Ogburn, *l.c.*; H. Wölbling, *l.c.*

[3] Under similar conditions ruthenium gives a green to blue solution—L. Wöhler and L. Metz, *Zeit. anorg. Chem.*, **138**, 368, 1924.

[4] L. Wöhler and L. Metz, *l.c.*; H. Remy, *Zeit. angew. Chem.*, **39**, 1061, 1926; S. C. Ogburn, *l.c.*; H. Wölbling, *l.c.*

[5] H. Wölbling and B. Steiger, *Mikrochem.*, **15**, 295, 1934. For other colour reactions of osmium and ruthenium, see B. Steiger, *ib.*, **16**, 193, 1935.

[6] A. Levol, *Ann. Chim. Phys.*, (3), **30**, 356, 1850; U. Antony and A. Lucchesi, *Gazz. Chim. Ital.*, **19**, 545, 1889; **20**, 601, 1890; **26**, ii, 350, 1896; L. Hoffmann and G. Krüss, *Ber.*, **20**, 2369, 2704, 1887; W. Bettel, *Chem. News*, **56**, 133, 1887; J. Riban, *Bull. Soc. chim.*, (2), **28**, 241, 1877; W. Langhuth, *Oester. Zeit. Berg. Hütten.*, **41**, 148, 1893.

[7] A. Ditte, *Compt. rend.*, **120**, 320, 1895; U. Antony and A. Lucchesi, *Gazz. Chim. Ital.*, **26**, ii, 350, 1896. For the action of alkali sulphides on silver sulphide, see A. Ditte, *Compt. rend.*, **120**, 91, 1895.

[8] To facilitate subsequent filtration, R. Gaze (*Apoth. Ztg.*, **27**, 959, 1912) adds not less than 0·5 nor more than 10 per cent. of mercuric chloride and warms up to 80° or 90° before and after "gassing" the solution.

What has here been stated with respect to gold sulphide might be repeated for platinum sulphide. The solubility of platinum sulphide in ammonium or sodium monosulphide is facilitated by the presence of arsenic and other sulphides.[1]

On account of the difficulty involved in separating gold and the platinum metals from the other members of the hydrogen sulphide group, it is best to separate these elements before precipitating the hydrogen sulphide group; or to redissolve the hydrogen sulphide precipitate in acids and separate the gold and platinum metals from the solution of the sulphides. To precipitate gold and platinum, advantage is taken of the ease with which their compounds are reduced to the metal. Various reducing agents are available: sulphurous acid,[2] oxalic acid,[3] ferrous chloride (or sulphate),[4] hydrazine hydrochloride (or sulphate),[5] hydroxylamine hydrochloride,[6] alkaline formaldehyde solutions,[7] alkaline hydrogen peroxide solutions,[8] chloral hydrate,[9] magnesium,[10] nickel,[11] hypophosphorous acid,[12] cane sugar,[13] benzidine,[14] and other reagents.[15]

Sulphurous acid, oxalic acid and hydrazine hydrochloride are most convenient. The choice of the right precipitating agent is determined by the nature of the accompanying elements. The precipitation of gold by these reducing agents generally leads to low results. For instance, Hoffmann[16] found:

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[1] V. N. Ivanov, *Journ. Russ. Phys. Chem. Soc.*, 48, 527, 1916.

[2] P. Berthier, *Ann. Chim. Phys.*, (3), 7, 82, 1843; V. Lenher, *Journ. Amer. Chem. Soc.*, 35, 546, 1913; M. E. Diemer, *ib.*, 35, 552, 1913.

[3] L. Hoffmann and G. Krüss, *Liebig's Ann.*, 238, 66, 1887; *Chem. News*, 56, 83, 1887; A. Béchamp and C. St Pierre, *Compt. rend.*, 52, 757, 1861; *Chem. News*, 4, 284, 1861; M. Wunder and V. Thüringer, *Zeit. anal. Chem.*, 52, 660, 1913.

[4] L. Hoffmann and G. Krüss, *Liebig's Ann.*, 238, 66, 1887; *Chem. News*, 56, 83, 1887; L. Hoffmann, *Untersuchung über das Gold*, Erlangen, 11, 1887.

[5] P. Jannasch and O. von Mayer, *Ber.*, 38, 2129, 1905; A. Christensen, *Zeit. anal. Chem.*, 54, 158, 1915; *Archiv pharm. Chem.*, 22, 105, 1915 (gold is reduced in the cold, platinum with heat); I. N. Plaksin and M. A. Koyukhova, *Tzvetnuie Metal.*, 6, 35, 1931; *Chim. et Ind.*, 27, 1086, 1932.

[6] C. Winkler, *Ber.*, 22, 890, 1889; A. Lainer, *Monats.*, 12, 639, 1891; P. Jannasch and O. von Mayer, *Ber.*, 38, 2129, 1905.

[7] L. Vanino, *Ber.*, 31, 1763, 1898; *Zeit. Chem. Ind. Koll.*, 1, 272, 1906; V. Lenher, *Journ. Amer. Chem. Soc.*, 35, 546, 1913; J. A. Muller and A. Foix, *Bull. Soc. chim.*, (4), 33, 717, 1922. For formic acid, see W. Bettel, *Chem. News*, 56, 133, 1887; V. Lenher, *loc. cit.*; W. Oechsner de Coninck and W. Chauvenet, *Ann. Chim. anal.*, 21, 114, 1914.

[8] Mutual reduction.—L. Vanino and L. Seemann, *Ber.*, 32, 1968, 1899; *Chem. News*, 82, 70, 1900; L. Rössler, *Zeit. anal. Chem.*, 49, 739, 1910; P. Drawe, *Zeit. angew. Chem.*, 33, 272, 1920.

[9] P. J. Dirvell, *Bull. Soc. chim.*, (2), 46, 806, 1886.

[10] C. Scheibler, *Ber.*, 2, 295, 1869; A. Villiers and F. Borg, *Compt. rend.*, 116, 1524, 1893.

[11] V. Goldschmidt, *Zeit. anal. Chem.*, 45, 87, 1906.

[12] F. Treubert, Dissertation, München, 1909; L. Moser and M. Niessner, *Zeit. anal. Chem.*, 63, 240, 1923.

[13] P. Leidler, *Zeit. Chem. Ind. Koll.*, 2, 103, 1907.

[14] G. Malatesta and E. di Nola, *Boll. chim. farm.*, 52, 461, 1913.

[15] For lactic acid, acetone, phenol and aniline in alkaline solution, and pyrogallol and quinol in acid solution, see V. Lenher, *Journ. Amer. Chem. Soc.*, 35, 546, 1913; F. E. Beamish, J. J. Russell and J. Seath, *Ind. Eng. Chem. Anal. Ed.*, 9, 174, 1937; J. Seath and F. E. Beamish, *ib.*, 9, 373, 1937; F. E. Beamish and M. Scott, *ib.*, 9, 460, 1937; for tetraethyl-ammonium iodide, see J. L. Maynard, *ib.*, 8, 368, 1936. For mercuric iodide, see D. Nider, *Koll. Zeit.*, 44, 139, 1928. For the micro-volumetric determination of gold by precipitation with quinol, see W. B. Pollard, *Analyst*, 62, 597, 1937.

[16] L. Hoffmann, *Untersuchung über das Gold*, Erlangen, 11, 1887; E. Pfiwoznik, *Oester. Zeit. Berg. Hütt.*, 59, 639, 1911; W. Langhuth, *ib.*, 41, 148, 1893; W. Bettel, *Chem. News*, 56, 133, 1887.

Table LII.—Comparison of Different Precipitating Agents for Gold.

Precipitating agent.	Gold taken.	Gold found.	Per cent. loss.
Sulphurous acid . .	3·12360	3·11916	0·14
Sulphurous acid . .	2·14739	2·14688	0·03
Oxalic acid . . .	2·15292	2·15040	0·12
Ferrous chloride . .	1·65596	1·65535	0·04

This loss arises from the fact that the gold is precipitated in a very fine state of subdivision and minute particles of gold pass through the filter-paper. In consequence, it is best to work with solutions as concentrated as possible and to let the mixture stand in contact with the acid mother liquid for some time in a warm place, agitating the solution thoroughly from time to time. This treatment favours the coagulation of the particles of gold and thus facilitates "clean" filtrations.[1]

Precipitation by Sulphurous Acid.—The acid solution under investigation is concentrated on a water bath until crystals begin to form as a drop of the solution is cooled on the end of a glass rod. Add sufficient water to dissolve all the crystals [2] and digest the solution for half an hour on a water bath with an excess of sulphurous acid. At the end of that time the liquid should be clear and smell of sulphur dioxide. The addition of sulphur dioxide from time to time may be necessary. The solution is then filtered and the metallic gold washed with dilute hydrochloric acid and ignited in a weighed porcelain crucible.

This precipitating agent is superior to both oxalic acid and ferrous chloride. There is no danger of loss by spurting, as occurs with oxalic acid, which decomposes with the formation of carbon dioxide; and the precipitated gold is more easily washed free from salts than is the case when ferrous salts are used. The time needed for complete precipitation—half an hour—is shorter than that needed for complete precipitation with oxalic acid or ferrous chloride. If selenium be present, it will be precipitated with the gold. If platinum be present and the solution be not sufficiently acid, the precipitated gold will be contaminated with platinum, and the results for gold will then be a little high. Oxalic acid, however, gives the best separations of gold from platinum, although in separating gold from platinum it is usual first to precipitate the latter metal as ammonium or potassium chloroplatinate. Sulphurous acid gives better separations of gold from palladium than ferrous chloride or oxalic acid, while there is little to choose between these three agents for the separation of gold from iridium, rhodium and ruthenium.

A large excess of hydrochloric acid generally retards the precipitation of gold. Nitric acid is, naturally, supposed to be absent; this is removed by

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[1] J. Volhard (*Liebig's Ann.*, 198, 331, 1879) recommends warming the gold solution with mercuric oxide on the water bath. The particles of gold are said to aggregate with the mercuric oxide and are, in consequence, easily filtered and washed. The mercuric oxide volatilises on ignition.

[2] The gold chloride may be partially decomposed into metallic gold during the evaporation. This does not matter.

repeated evaporation with hydrochloric acid.[1] No notice need be taken of any separation of gold during the evaporation.

Precipitation by Oxalic Acid.—The solution is concentrated as described above, and the acid solution is neutralised and warmed with oxalic acid, until further additions of oxalic acid give no further separation of gold.[2] The reduction is best made in a covered vessel, on account of the risk of losses by the spurting which attends the oxidation of the oxalic acid to carbon dioxide. The vessel is allowed to stand in a warm place for about 24 hours, and the metallic gold is filtered, washed with water,[3] ignited in a porcelain crucible and weighed as metallic gold.

The oxalic acid process is not satisfactory in the separation of gold from palladium, since some of the palladium is precipitated with the gold—about 0.5 per cent. is precipitated. When lead is present, it will be precipitated as oxalate with the gold. Hence the lead must be removed or another precipitating agent must be substituted. If the lead be removed as sulphate, there is a danger of the latter carrying down some of the gold. If much lead and little gold be present, probably all the gold will be found with the precipitate of lead sulphate.[4] Selenium and molybdenum are not precipitated; but if insufficient hydrochloric acid be present, tellurium, if present, may give a precipitate which is removed from the gold by washing with hydrochloric acid. If much copper be present, the gold will be contaminated with copper oxalate, even if a great excess of hydrochloric acid be used. To separate the gold from the copper oxalate, Purgotti[5] proposes the following process:—Evaporate the aqua regia solution on a water bath to dryness, dissolve the residue in water, add oxalic acid and digest the mixture in a warm place for 48 hours. Neutralise the boiling solution with potassium hydroxide. If a great excess of oxalic acid has not been added, more will be needed so as to form a soluble double copper and potassium oxalate, which imparts an ultramarine blue tint to the solution. The precipitated gold can then be filtered from the solution and washed in the usual manner. When the above-mentioned disturbing elements are present, it is best to use the sulphurous acid or the hydrazine process.[6]

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[1] It is interesting to observe in this connection that *the evaporation of alkali nitrates to dryness a number of times with hydrochloric acid is not sufficient to effect the complete conversion of the nitrates to chlorides.* For instance, 0.1893 grm. of potassium nitrate gave after a number of evaporations:

Evaporation	First.	Second.	Third. . . . Ninth. . . . Twelfth.
Potassium nitrate .	0.1136	0.0581	0.0149 . . . 0.0013 . . . 0.0013 grm.

B. Lucanus (*Zeit. anal. Chem.*, 3, 403, 1864) prefers to ignite the alkali nitrate with four to six times its weight of grape sugar, so as to form the carbonate; and when this is treated with hydrochloric acid, the chloride will be obtained free from the nitrate.

[2] Note that most of the oxalates (excepting those of the alkalies and magnesium) are but sparingly soluble in neutral and feebly acid solutions. Some dissolve in alkalies and all dissolve in concentrated mineral acids, while some are almost insoluble in dilute acids—*e.g.* copper oxalate in dilute nitric acid (C. Luckow, *Zeit. anal. Chem.*, 26, 9, 1887; *Chem. News*, 55, 73, 1887; G. Bornemann, *Chem. Ztg.*, 23, 565, 1899; H. L. Ward, *Zeit. anorg. Chem.*, 77, 257, 269, 1912)—hence, when other metals are present, the solution should be sufficiently acid to prevent the separation of insoluble oxalates.

[3] If some of the less soluble oxalates be present, they can be removed by washing the precipitated gold with dilute hydrochloric acid.

[4] C. Whitehead, *Chem. News*, 66, 19, 1892.

[5] E. Purgotti, *Zeit. anal. Chem.*, 9, 128, 1870.

[6] R. Fresenius (*Quantitative Chemical Analysis*, London, 1, 477, 1876) says that the oxalic process is not satisfactory in the presence of lead, mercurous and silver salts. Since the determinations are usually made in hydrochloric acid solutions, if the solution be dilute, practically all the silver will be precipitated as chloride. Mercurous salts cannot remain in contact with gold trichloride without reducing the latter, so that if mercury and gold are present together in solution, the mercury must be in the higher state of oxidation.

Precipitation by Hydrazine Hydrochloride.—Hydrazine hydrochloride may be used to precipitate gold from neutral, acid or alkaline solutions containing potassium, sodium, barium, strontium, calcium, magnesium, aluminium, chromium, zinc, manganese, iron, uranium, nickel, cobalt, cadmium, mercury, lead, copper, but not tin.[1]   When platinum metals are associated with the gold in a solution, the gold may be first precipitated by adding hydroxylamine hydrochloride to the solution acidified with hydrochloric acid and digesting the mixture on a water bath for some time.   The filtrate must be tested to make sure that all the gold is precipitated, because hydroxylamine hydrochloride is not so vigorous an agent as the hydrazine salt.   The palladium, iridium, platinum, rhodium and osmium remain in solution.   The first four elements, if present, are precipitated by hydrazine hydrochloride in alkaline solution, but not in acid solutions.[2]

§ 231. The Separation of Gold and Platinum from Tin, Arsenic and Antimony.

The tin group of elements cannot be quantitatively separated from the gold-platinum group by reducing agents; nor can tin be dissolved from the platinum metals by treatment with acids; and the sulphides cannot be separated by concentrated hydrochloric acid nor by sodium hydroxide.   The volatilisation of tin sulphide in a stream of hydrogen sulphide is tedious and slow.   The chlorides of tin, antimony and arsenic can be volatilised in a stream of chlorine or hydrogen chloride.   The volatilisation of the bromides in a stream of bromine gives better results.

Volatilisation Process.—Transfer the washed sulphides to a porcelain boat along with the filter-paper ash.[3]   Place the boat *B* in a hard glass combustion tube and pass a stream of dry bromine or hydrogen chloride through the tube while the boat is heated as indicated in fig. 104.   The exit tube leads into an absorption flask *A* containing dilute hydrochloric acid.   The bromides or chlorides of arsenic, antimony and tin volatilise and are retained in the absorption flask; any sublimate in the tube is driven away from the boat by means of the naked flame from a Bunsen burner.   The gold and platinum remain in the boat.[4]   The combustion tube is washed with dilute hydrochloric acid and the washings run into the absorption flask.   The tin, arsenic and antimony in the latter can be determined in the usual manner.   The process is accurate but it occupies a long time.

Dirvell's Process.[5]—Dissolve the precipitated sulphides in aqua regia.   Add a small quantity of a saturated neutral solution of sodium oxalate and of oxalic acid.   Then add a considerable excess of sodium hydroxide—pure by alcohol. No notice need be taken of any separation of sodium oxalate.   Heat the

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[1] In acid solution, mercury and copper may be partially precipitated, and platinum after it has been reduced to the dichloride—A. Christensen, *Zeit. anal. Chem.*, **54**, 158, 1915.

[2] Osmium and ruthenium are only partially precipitated in alkaline solution by the hydrazine salt and not at all in acid solutions.

[3] The filter-paper is separated from the sulphides and burned alone.   The sulphides may also be intimately mixed with 3–5 times their weight of ammonium chloride and their own weight of ammonium nitrate and calcined.   The gold and platinum remain in the crucible.

[4] R. Fresenius, *Zeit. anal. Chem.*, **25**, 200, 1886; L. Wöhler and A. Spengel, *ib.*, **50**, 165, 1911; L. L. de Koninck and A. Lecrenier, *Rev. Univ. Mines*, (3), **2**, 98, 1888; L. Elsner, *Journ. prakt. Chem.*, (1), **35**, 310, 1845; A. Béchamp and C. St. Pierre, *Compt. rend.*, **52**, 757, 1861; P. de Clermont, *ib.*, **88**, 972, 1879; G. Campari, *Ann. di Chim.*, (3), **74**, 1, 1882; T. Bailey, *Journ. Chem. Soc.*, **49**, 735, 1886; U. Antony and L. Niccoli, *Gazz. Chim. Ital.*, **22**, ii, 408, 1892.

[5] P. J. Dirvell, *Bull. Soc. chim.*, (2), **46**, 806, 1886.

solution to boiling and while boiling add, drop by drop, a solution of chloral hydrate. Boil the solution under a hood.[1] When an excess of chloral hydrate has been added and the gold and platinum have precipitated, filter the boiling solution, wash and weigh the mixed metals in the usual manner. The filtrate is diluted with water and boiled to drive off the chloroform. The antimony,
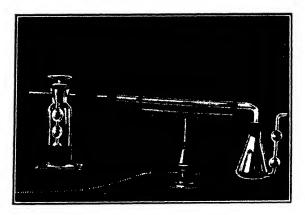
FIG. 104.—The Separation of the Tin from the Gold-Platinum Group.

arsenic and tin are determined in the filtrate in the usual manner. The washed gold and platinum are dissolved in aqua regia and separated either by precipitating the gold with oxalic acid, or the platinum with ammonium chloride (page 475).

§ 232. The Colorimetric Determination of Gold.

Gold can be determined, somewhat approximately, by the tint obtained when gold solution is brought in contact with a solution containing a mixture of stannous and stannic chlorides.[2] The gold sulphide is dissolved in 10 c.c. of aqua regia (three volumes of concentrated hydrochloric acid and one volume of concentrated nitric acid), and treated with a saturated solution of stannous chloride until the yellow colour is bleached. The purple tint which develops in less than a minute is compared with a set of artificial standards, made by mixing solutions of copper and cobalt salts in the required proportion. A coloration is obtained when but one part of gold per million parts of solution is present. The usual precautions for colorimetric determinations are here of exceptionally great importance in order to get reliable results. The difficulty in controlling

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[1] Vapours of chloroform are evolved.

[2] E. Sonstadt, *Chem. News*, 26, 159, 1872; T. K. Rose, *ib.*, 66, 271, 1892; R. N. Maxon, *Amer. J. Science*, (4), 21, 270, 1906; *Chem. News*, 94, 257, 1906; A. Carnot, *Compt. rend.*, 97, 105, 1883; J. Moir, *Journ. Chem. Met. Min. Soc. S. Africa*, 4, 125, 1903; A. Prister, *ib.*, 4, 235, 1903; H. R. Cassel, *Eng. Min. Journ.*, 76, 661, 1903; E. Rupp, *Ber.*, 36, 3961, 1903; M. E. Pozzi-Escot, *Ann. Chim. anal.*, 12, 90, 1907; W. Bettel, *Min. Eng. World*, 35, 987 1911. For the detection of traces of gold, see J. E. Saul, *Analyst*, 38, 54, 1913; C. B. Brodigan, *Met. Chem. Eng.*, 12, 460, 1914; J. A. Muller and A. Foix, *Bull. Soc. chim.*, (4), 33, 717, 1922; D. Nider, *Koll. Zeit.*, 44, 139, 1928. J. A. Muller and A. Foix (*l.c.*) obtain a colloidal solution of gold for colorimetric comparison by reducing the alkaline solution with formaldehyde; see also T. Itó, *Journ. Chem. Soc. Japan*, 58, 288, 1937. D. Nider (*l.c.*) says that mercuric iodide and excess potassium iodide in alkaline solution is better than stannous chloride.

the exact tint of the "purple of Cassius," thus formed, considerably limits the scope of this process.[1]

§ 233. The Analysis of Colours containing Purple of Cassius.

In the analysis of gold colours—which usually contain lead oxide, silver carbonate, stannic oxide, gold, boric oxide, silica and soda—the sodium peroxide fusion (pages 264 and 527) is an excellent method of opening up the compound. One portion of the sample is fused in a porcelain crucible and the resulting cake is used for the determination of gold, silver, tin and lead. The boric oxide is determined in another portion of the sample fused in a silver crucible. The alkalies are determined by the method described on page 214; the ignition is conducted in a silver crucible. The silica and alumina are determined on another portion of the sample fused in a silver crucible. The separation of the gold, silver, lead and tin alone requires special mention.

Separation of Silver.—The fused cake is taken up with water and the solution warmed with an excess of hydrochloric acid. The gold passes into solution as gold chloride,[2] the silver is precipitated as silver chloride along with a certain amount of silica and lead. The solution is diluted, so that it contains no more than the equivalent of 0·25 to 0·30N-HCl after the alkali has been neutralised. The hot solution is filtered through a hot-jacketed funnel, and washed with 0·25N-hydrochloric acid. The precipitated silver chloride is freed from silica by treatment with hydrofluoric acid, and then dissolved in ammonia.[3] The properties of silver chloride should here be studied—page 745.

Purification of Silver Chloride from Lead Chloride.—The lead chloride can be removed from the ammoniacal solution of silver chloride by adding 5 c.c. of a concentrated solution of ammonium nitrate and 40 c.c. of a 2 per cent. solution of hydrogen peroxide per 25 c.c. of the cold ammoniacal solution.[4] In 3 or 4 hours the yellowish-brown flocculent precipitate of lead peroxide may be filtered and washed, first with dilute ammonia and lastly with cold water. The lead peroxide is dissolved in nitric acid, assisted by the addition of a little hydrogen peroxide. The lead is transformed into sulphate and weighed in the usual manner. The silver is determined by acidifying the solution with nitric acid and boiling it for a short time. The precipitated silver chloride is filtered as indicated on page 747.

Separation of Tin.—The filtrate remaining after the removal of the silver chloride contains the gold, lead and tin. These metals are precipitated as sulphides by means of hydrogen sulphide. The sulphides are washed as indicated on page 315, and dried. The paper is ignited after the sulphides have been transferred to a porcelain boat. The ash of the filter-paper is also brushed

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[1] For volumetric methods of determining gold, see V. Lenher, *Journ. Amer. Chem. Soc.*, 35, 733, 1913; L. Vanino and F. Hartwagner, *Zeit. anal. Chem.*, 55, 377, 1916; H. Peterson, *Zeit. anorg. Chem.*, 19, 59, 1898; E. Müller and F. Weigbrod, *ib.*, 156, 17, 1926; 169, 394, 1928; E. Müller and R. Bennewitz, *ib.*, 179, 113, 1929; E. Müller and W. Stein, *Elektrochem. Zeit.*, 36, 376, 1930; E. Zintl, *ib.*, 36, 551, 1930.

[2] Although hydrogen peroxide in alkaline solution precipitates metallic gold, the hydrogen peroxide in the presence of hydrochloric acid forms chlorine, which dissolves the gold as chloride. The tin is in the form of stannic chloride, and stannic chloride gives no precipitate with gold chloride.

[3] It is sometimes difficult to dissolve all the silver chloride in ammonia. In that case, successive treatment of the precipitate on the filter-paper with ammonia, boiling water and dilute nitric acid will bring about the solution of the silver chloride.

[4] P. Jannasch, *Ber.*, 26, 1496, 1893.

into the boat and the tin volatilised by heating the boat in a stream of bromine (fig. 104).[1]

Separation of Gold and Lead. – The boat containing the gold and lead bromides is again introduced into a combustion tube and heated in a current of hydrogen gas with the usual precautions against explosion. Metallic gold and lead remain in the boat. The latter is alone soluble in dilute nitric acid, hence the separation is easy. Precipitate the lead, in the nitric acid filtrate from the gold, as sulphate. Add the weight of lead sulphate so obtained to the lead sulphate obtained from the silver and compute the corresponding amount of lead oxide in the usual way. The gold is ignited, weighed and reported as metallic gold.

The amount of gold in these colours is relatively small and there is a slight loss of gold with each precipitation. The silver and gold are best determined by the fusion, cupellation and parting processes on a separate sample, and the tin and lead by usual processes. In illustration, the analysis of a purple of Cassius colour gave:

SiO_2.	Al_2O_3.	SnO_2.	Na_2O.	Ag.	PbO.	Au.	B_2O_3.	CO_2.
15·10	1·21	30·19	4·49	7·00	29·23	1·44	10·50	1·20 per cent.

The carbon dioxide is determined by the method of page 625.

Mylius' Ether Process.[2]—When acidified aqueous solutions of gold chloride in presence of many other chlorides are treated with ether, the ethereal solution which floats on the aqueous layer carries most of the gold chloride and the chlorides of the other metals remain below in the aqueous layer. When 100 c.c. of ether were shaken with 100 c.c. of an aqueous solution containing the equivalent of 1 grm. of metal, Mylius found that the following percentage amounts passed into the ethereal solution:

	$HgCl_2$.	$AuCl_3$.	$FeCl_3$.	$SbCl_3$.	$SnCl_4$.	$AsCl_3$.
10 per cent. HCl . .	0·4	98·2	8	22	23	7·3
1 per cent. HCl . .	13·0	85·0	tr.	0·3	0·8	0·2

and 3·0 per cent. of $TeCl_4$; 0·05 $CuCl_2$; 0·03 $ZnCl_2$; 0·01 $NiCl_2$; 0·01 $PtCl_4$; 0·01 $PdCl_2$; 0·02 H_2IrCl_6 from the 10 per cent. acid solutions, and only traces from the 1 per cent. acid solutions. No lead or silver chloride, was dissolved by the ether. Hence, by treating a solution of gold chloride containing 5–10 per cent. of gold and 5–10 per cent. of free hydrochloric acid (HCl) four or five times with ether in a separating funnel, or in the apparatus, figs. 108 or 110, very good separations are said to be effected. The ether is distilled off and the gold reduced with sulphurous acid. The method promises to be useful for the separation of gold from certain metals.

§ 234. The Determination of Gold and Silver by Cupellation and Parting.

The fusion and cupellation are performed very much as indicated on page 336, but some modifications must be introduced.[3] The powdered sample

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[1] If bismuth be present, it will be volatilised with the tin, and the separation of bismuth and tin can be effected by the usual methods.

[2] F. Mylius, *Zeit. anorg. Chem.*, **70**, 203, 1911; F. Mylius and C. Huttner, *Ber.*, **44**, 1315, 1911.

[3] E. A. Smith, *Inst. Min. Met.*, **9**, 315, 1901; *Chem. News*, **84**, 62, 74, 89, 98, 134, 1901; **93**, 225, 1906; *The Sampling and Assay of the Precious Metals*, London, 1913; R. King, *Min. Scient. Press*, **110**, 917, 1915; F. P. Dewey, *Journ. Ind. Eng. Chem.*, **6**, 650, 728, 1914. "Gold lustres" or "liquid gold" can be prepared for cupellation by evaporating a weighed quantity in a porcelain dish, and incinerating the carbonaceous residue to drive off the carbon. The residue may be dissolved in aqua regia and analysed by the wet process, or wrapped in sheet lead and cupelled for gold and silver.

should be thoroughly mixed with the flux, so that as soon as the lead is reduced it may come into contact with the gold and silver.[1] The lead dissolves these metals, and the alloy finally collects at the bottom of the crucible. The amount of reducing agent added to the fusion mixture should be proportioned to give a button weighing about 30 grms. The sample under investigation may be reducing, oxidising or neutral, and too much or insufficient lead may be obtained.

Preliminary Assay.—It is therefore necessary to make a preliminary assay by fusing an intimate mixture of 5 grms. of the powdered sample with:

Litharge, 50 grms.; sodium bicarbonate, 18 grms.; calcined borax, 5 grms.

The mixture is placed in a crucible of such a capacity that the crucible is less than three-fourths filled, and covered with a layer of common salt.[2] The fusion is made as indicated on page 336. Break the cold crucible, if the molten mixture has not been poured into a mould. Hammer off the slag and weigh the button. The button from 30 grms. of the sample should weigh between 16 and 20 grms. Hence the button from the 5 grms. of the sample should weigh about 3 grms. Weigh the button. Suppose:

(1) The button weighs nearly 3 grms. In that case the above-mentioned mixture is the right one. Hence fuse 30 grms. of the sample with

Litharge, 50 grms.; sodium bicarbonate, 18 grms.; calcined borax, 5 grms.

in a suitable crucible. The mixture is covered with a layer of common salt as indicated on page 336.

(2) The button weighs over 3 grms. The sample is therefore a strong reducing agent and this must be corrected by the addition of an oxidising agent, say, nitre. Too large a button gives low results for silver, since some silver is then lost owing to absorption by the cupel and by volatilisation, and this the more the greater the amount of lead present.

EXAMPLE.—Suppose that the button weighs 7 grms. Then 30 grms. of sample would give a button weighing 42 grms., that is, 24 grms. too much lead. Since 1 grm. of nitre oxidises about 2 grms. of lead, it will be obvious that $\frac{1}{2}$ of 24 = 12 grms. of nitre must be used with the mixture indicated in (1).

(3) If the weight of the button be less than 3 grms., the sample has but a slight reducing action, which is not sufficient to give a button of normal weight. There is then a danger of some gold and silver being left in the slag. A little reducing agent—charcoal or argol (crude acid potassium tartrate)—must then be added to the mixture indicated in (1).

EXAMPLE.—Suppose the button weighed 2 grms., the button from 30 grms. of the sample would weigh 2 × 6 = 12 grms. Hence, in order to get a button weighing 18 grms., enough reducing agent to give 6 more grms. of lead is needed. One grm. of argol is found to reduce 10 grms. of lead from litharge. Hence it is necessary to add $\frac{1}{10}$ of 6 = 0·6 grm. of argol to the mixture indicated in (1).

(4) If no button is obtained, the sample is either neutral or oxidising. In the former case, the fusion can be made with 2 grms. of argol, 30 grms. of the

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[1] It is most convenient to mix the charge in the crucible. The fluxes are placed in the crucible with the bulkiest one at the bottom. The accurately weighed sample is put on the top of the fluxes and the whole most thoroughly mixed with a spatula.

[2] Previously fused and ground to powder. The practice of using a salt or borax cover on the charge is not so common as it was and normally it is unnecessary. When a salt cover is used with rich ores, there is some danger of the formation of volatile chlorides of silver and gold.

sample and the normal fusion mixture. If the sample be oxidising, the button may still be too small. In that case, the weight of the button obtained will furnish data for calculating how much more argol will be required to give a button of normal weight.

Example of Assay.—The preliminary fusion of a sample of gold colour showed no button of lead, and the fusion of 30 grms. of the sample with 50 grms. of litharge, 1·5 grms. of argol, 18 grms. of sodium bicarbonate and 5 grms. of calcined borax gave a button weighing just less than 20 grms.

If the charge in the crucible contains much nitre and uncalcined borax, it is liable to froth over. To prevent this, start the fusion at a low temperature and raise the temperature very slowly. If the bubbling be still troublesome, it may be advisable to roast the sample in a shallow clay "roasting dish" in the muffle, and take portions of the roasted sample for the preliminary and final assay. The final results must of course be expressed in terms of the roasted sample.

We may now assume that the fusion and the cupellation have been performed as indicated on page 336. The bead of silver and gold is weighed.[1] The separate determination of the gold and silver involves the two operations of inquartation and parting.[2]

Inquartation and Parting.—The latter term is applied to the process of separating gold and silver by the action of acid on the bead or "prill" obtained during cupellation. Nitric or sulphuric acid may be used, but the former is almost universally employed. If an alloy of silver and gold be digested with nitric acid, silver, not gold, is dissolved. It is necessary that at least twice as much silver as gold be present to ensure the dissolution of all the silver by nitric acid of specific gravity not less than 1·26, after boiling for half an hour. But, as a matter of fact, in parting all bullion assays, five times as much silver as gold is considered necessary. For successful parting, therefore, special attention must be paid to:

(1) The concentration of the nitric acid. For general work, an acid of the strength recommended by Keller [3] may be used, namely, 1 part of concentrated nitric acid (sp. gr. 1·42) with 9 parts of distilled water. With this acid, Keller says the gold remains as a coherent mass, even if 500 times as much silver as gold be present. The beads are supposed to be boiled in the acid about 15 minutes. There are, however, certain advantages in using acids of two different strengths, as indicated below.

(2) The temperature of the acid. The acid should be boiling when the bead to be parted is dropped into the flask. If the bead be dropped into cold acid and then heated up to the boiling-point, the gold is liable to disintegrate into a finely divided condition—especially if the proportion of silver is large— and this may lead to loss in subsequent operations.

(3) The ratio of silver to gold in the bead. Although the ratio 5 : 1 is usually recommended, this is not quite under control. If less than this amount of silver be present, more silver can be added to the crucible when the fusion is made for the cupellation; or to the lead button during cupellation when gold alone, and not silver, is to be determined. If silver and gold are to be determined, the bead, after cupellation, is weighed. This weight represents silver + gold. A small piece of pure sheet lead weighing about 2 grms. is folded in the shape of a hollow cone. The necessary amount of pure silver, together

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[1] E. J. Hall, *Eng. Min. Journ.*, 100, 149, 1915.

[2] The "gold" obtained by burning "gold rags" from the "decorating shop" of a pottery is evaluated in this way.

[3] E. Keller, *Trans. Amer. Inst. Min. Eng.*, 36, 3, 1905.

with the bead, is placed in the cone, which is then closed and folded into a little packet. This is then cupelled. Instead of this recupellation, some prefer to alloy the silver with the bead by fusion on charcoal before the blowpipe. The latter operation requires some practice for successful work. The process for alloying silver with the cupelled bead in order to prepare it for parting is called "inquartation," because formerly at least three parts of silver to one of gold were considered necessary for successful parting.

With practice, the amount of silver needed can be estimated from the colour of the bead. If the bead is white, it contains more than three parts of silver to one of gold, and inquartation may be unnecessary, or the bead may be inquarted with its own weight of silver. If the bead is greenish-yellow, it probably contains less than three parts of silver to one of gold, and the bead is inquarted with about twice its weight of silver. If the bead is yellow or reddish-yellow, the gold predominates and it is inquarted with two or three times its weight of silver. A set of standard prills can be easily made for comparison.

The "quarted" alloy is removed from the cupel with the "bead forceps," cleaned with the "button brush," and hammered on an anvil to a flat disc about 1 mm. thick. The metal becomes hard and brittle during the hammering, and the disc is accordingly annealed by heating it to dull redness while supported on a clean cupel, and cooling it rapidly on a piece of brass foil. The bead is then rolled between two steel rollers so as to form a long strip. If the disc were rolled without annealing, the edges of the strip would probably be rough and little pieces would drop off during the action of the acid. The strip is again annealed and rolled down to a thickness of about 0·15 mm.[1] The roll is placed in a small parting flask[2] containing about 30 c.c. of nitric acid[3] (sp. gr. 1·06–1·12), previously heated to about 90°. The acid is boiled[4] for about 20 minutes; cooled; and decanted off. The roll is washed twice with distilled water. 30 c.c. of boiling concentrated nitric acid (sp. gr. 1·3)[5] are then added to the flask containing the roll. After 20 minutes' boiling,[6] decant off the acid, and wash three times by decantation with distilled water.[7] Fill the flask to the very top with distilled water, and place a close-fitting porcelain capsule—"parting cup"—over the mouth of the flask. Invert the flask (fig. 105). The roll settles in the parting cup. The flask is removed by raising its mouth to the level of the water in the capsule and quickly moving the flask at right angles away from the parting cup to allow the water to run away. The water is decanted from the parting cup. The cup and contents

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[1] A. Hackl (*Chem. Ztg.*, **57**, 723, 1933) says that the strip should also be annealed before parting, as higher values for gold are thereby obtained.

[2] There are several different forms. The flasks are better without a lip. Some prefer to conduct the parting in small glazed porcelain crucibles. The "cupping" described in the text is then unnecessary.

[3] Free from chlorine, sulphuric and sulphurous acids and sulphides.

[4] If the roll turns black and the action stops, insufficient silver is probably present. The roll is then coiled up and fused with two or three times its weight of silver and re-parted.

[5] Some prefer to use an acid of sp. gr. 1·26, made by diluting one volume of concentrated acid (sp. gr. 1·42) with an equal volume of water. J. W. A. H. Smit (*Rec. Trav. chim.*, **40**, 119, 1921) recommends an acid of 1·33 gravity. When very little gold is present, the first acid should not be above 1·06 gravity. According to A. Hackl (*Zeit. anal. Chem.*, **97**, 411, 1934), up to 0·02 per cent. of the gold may be lost during parting owing to the formation of nitrous acid. He says that the addition of 1 per cent. by volume of methyl alcohol lessens this loss.

[6] By first boiling with a dilute acid and afterwards with a more concentrated acid, the removal of the silver is more complete, the gold becomes more compact and there is less risk of disintegrating the residual gold.

[7] If the gold disintegrates, there will probably be losses in transferring.

are dried by holding the cup with a pair of tongs in the flame of a Bunsen burner until the cup is red-hot.[1]   The gold is annealed and changes from a soft dark brown condition to hard yellow gold.[2]   When cold, weigh (see page 473).   Subtract the weight of the gold so obtained from the weight of the original prill to get the approximate weight of silver in the given sample.
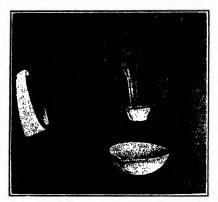
FIG. 105.—"Cupping."

Errors.—The errors in the cupellation process involve:—

(1) The retention of gold by the slag during fusion.—If the amount of collecting lead is ample, the error is not serious.[3]   Buttons less than about 20 grms. should not be used.   The loss is largely dependent on the nature of the impurities which pass into the slag.

(2) The loss of gold by volatilisation. —Gold and silver are both slightly volatile at high temperatures; hence they may be volatilised during fusion and cupellation.   The loss is greater the higher the temperature of cupellation.[4]   However, the loss due to this cause at the normal temperatures of the cupellation process is probably insignificant.

(3) The absorption of gold by the cupel.—The amount varies with the nature of the bone ash used in making the cupel.   The loss of gold is greater the higher the temperature of cupellation.[5]

(4) The retention of base metals by the cupelled beads.—A little lead is almost invariably retained by the bead cupelled at the regular temperatures. Hillebrand and Allen [6] found from 0·3 to 0·37 per cent. of lead with 0·09 grm. beads of gold.

(5) The solution of gold by the parting acid.—During parting a trace of gold appears to be dissolved by the nitric acid, even if it be free from hydrochloric acid or chlorine.   This amounts to about 0·01 to 0·03 per cent. on a half-gram bead.[7]

(6) The retention of silver by the parted gold.—The amount of silver which resists attack by the acid varies with the percentage of silver alloyed with the

[1] The drying must be carefully done or particles of gold may be spurted from the cup with the steam.   The drying may be done by placing the cup in the red-hot muffle for a short time.

[2] If the cup shows a black stain after it has been heated, the washing was imperfectly done and the analysis or assay should be repeated.   If, after parting, the amount of gold is more than one-third the weight of the bead, it must be fused with about three times its weight of silver and again parted.

[3] E. H. Miller and C. H. Fulton, *School Mines Quart.*, **17**, 160, 1896; W. F. Hillebrand and E. T. Allen, *Bull. U.S. Geol. Sur.*, **253**, 24, 1905.

[4] G. H. Makins, *Journ. Chem. Soc.*, **13**, 77, 1861; T. K. Rose, *ib.*, **63**, 707, 1893; J. Napier, *ib.*, **10**, 229, 1858; W. Witter, *Chem. Ztg.*, **23**, 522, 1889; H. Rössler, *Dingler's Journ.*, **206**, 189, 1884; W. F. Hillebrand and E. T. Allen, *Bull. U.S. Geol. Sur.*, **253**, 19, 1905; K. Friedrich, *Zeit. angew. Chem.*, **16**, 269, 1903; J. W. Richards, *Chem. News*, **74**, 2, 1896; W. Mostowitsch and W. Pletneff, *Met. Chem. Eng.*, **16**, 153, 1917; *Journ. Russ. Metall. Soc.*, 410, 1915.

[5] A. F. Crosse, *Journ. Chem. Met. Min. Soc. S.A.*, **2**, 325, 1902; T. L. Carter, *Eng. Min. Journ.*, **78**, 728, 1902; W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **253**, 19, 1905; J. Loevy, *Chem. Ztg.*, **38**, 82, 1914.

[6] W. F. Hillebrand and E. T. Allen, *Bull. U.S. Geol. Sur.*, **253**, 23, 1905.

[7] A. H. Allen, *Chem. News*, **25**, 85, 1872; V. Lenher, *Journ. Amer. Chem. Soc.*, **26**, 552, 1904.

gold to be parted.[1] It amounts to from 0·05 to 0·10 per cent. under ordinary conditions, and in the assay of gold bullion it is a minimum when the alloy contains about two parts of silver to one of gold. If more or less silver be present, the gold will be contaminated with more silver after parting. Other foreign elements, *e.g.* copper [2] and tellurium, may be retained by the bead.

(7) The occlusion of gases by the gold.— According to Graham,[3] about two parts by weight per 10,000 parts of gold are retained by the annealed gold. The amount depends upon the temperature of annealing.

Some of these errors obviously lead to low results, others to high results. Experience shows that under normal conditions both sets of errors are small, and tend to neutralise one another. The algebraic sum of the losses and gains is called the *surcharge*, and the surcharge can be approximately determined by control experiments with the purest available gold and silver. Since the purity, *i.e.* the fineness, of gold is usually reported in parts per 1000, a surcharge of +0·2 means that the gold actually reported weighed 0·2 part per 1000 more than was present; and conversely with a surcharge of −0·2.

It must be added that the greatest care must be exercised in weighing the gold. A balance even more sensitive than $\frac{1}{200}$ mgrm. is a distinct advantage. The precautions indicated in the first chapter require serious attention. Under favourable conditions, and weighing correctly to 0·01 per 1000, Rose [4] considers that the operations can be conducted with an error not exceeding ±0·02 part per 1000.

§ 235. The Determination of Platinum and the " Platinum Metals."

The metals of the platinum group are analysed with great difficulty. There is a difficulty in getting the metals into solution, for while palladium is dissolved by hot nitric acid and platinum by hot aqua regia, the other metals resist this solvent. The native metals may be alloyed in a form which resists attack by chemical agents, even aqua regia, most stubbornly. The platinum metals are sometimes stated to be precipitated by hydrogen sulphide from dilute acid solutions, and ruthenium, rhodium, palladium and osmium are further placed with those metals whose sulphides are insoluble in ammonium sulphide, and platinum and iridium with those whose sulphides are soluble in this menstruum. As a matter of fact, the precipitation of these metals in dilute acid solutions is not complete, and their behaviour towards ammonium sulphide is not sharp and definite. Fresenius,[5] for instance, says that the platinum metals are precipitated with difficulty by hydrogen sulphide and that the gas must be passed for a long time through hot solutions to bring down the sulphides. Antony and Lucchesi [6] say that hydrogen sulphide precipitates platinum completely as sulphide, PtS_2, from a 3 per cent. solution of hydro-

[1] W. F. Lowe, *Journ. Soc. Chem. Ind.*, **8**, 687, 1889; W. F. Hillebrand and E. T. Allen, *Bull. U.S. Geol. Sur.*, **253**, 25, 1905; T. K. Rose, *The Metallurgy of Gold*, London, 47, 1927.

[2] When the material under assay contains copper or antimony, these metals will pass into the button, and such buttons are difficult to cupel. When copper is present, the ratio of lead to copper should be at least 55 : 1.—J. W. A. H. Smit, *Rec. Trav. chim.*, **40**, 119, 1921.

[3] T. Graham, *Phil. Trans.*, **156**, 433, 1866.

[4] T. K. Rose, *Journ. Chem. Soc.*, **63**, 700, 1893; A. O. Watkins, *Chem. News*, **106**, 248, 259, 1912.

[5] C. R. Fresenius, *Anleitung zur qualitativen chemischen Analyse*, Braunschweig, 194, 500, 1885. For the precipitation of platinum as sulphide, see R. Gaze, *Apoth. Ztg.*, **27**, 959, 1912; *Chem. Zentr.*, (1), 464, 1913; V. N. Ivanov, *Journ. Russ. Phys. Chem. Soc.*, **48**, 427, 1916; R. Doht, *Zeit. anal. Chem.*, **64**, 37, 1924.

[6] U. Antony and A. Lucchesi, *Gazz. Chim. Ital.*, **26**, i, 211, 1896. See also I. Wada and S. Saito, *Bull. Inst. Chem. Research Tokyo*, **8**, 749, 1929.

chloroplatinic acid at 90°, but that at ordinary temperatures the precipitation is not complete and the composition of the precipitate varies—probably it is a decomposition product of a sulph-hydrate, $PtS(SH)_2$. With very dilute, cold solutions colloidal sulphide is formed. Similar remarks apply to palladium and iridium.[1] The behaviour of hydrogen sulphide towards all the ruthenium salts has not been fully investigated; salts corresponding with the tetroxide and perruthenic acid are completely precipitated, but the other ruthenium salts, as well as rhodium salts, are but imperfectly separated as sulphides.[2] Obviously, therefore, it cannot be assumed that hydrogen sulphide will precipitate the platinum metals from dilute acid solutions. In the treatment of the precipitated sulphides with ammonium sulphide iridium is not dissolved. Platinum sulphide is insoluble in ammonium sulphide but, if other sulphides be present—gold, tin, antimony, arsenic—some platinum may pass into solution; ruthenium sulphide, precipitated from salt solutions of the sesqui-oxide, is partly dissolved by the same menstruum. The behaviour of the precipitated sulphides is also partly influenced by the conditions of precipitation, e.g. hot or cold solutions. If rhodium be precipitated from hot solutions in the presence of gold, the gold sulphide is virtually insoluble in ammonium sulphide.

The Cupellation Process for Gold, Silver and Platinum.—When gold is determined by the process described in the preceding section, the bead will have a greyish colour if small amounts of platinum be present[3]; and if larger amounts be present, the bead will have a rough "frosted" appearance, because it "freezes" before all the lead is oxidised. The method used for separating platinum, under these conditions, depends on the solubility of platinum in nitric acid when the metal is alloyed with at least 12 times its weight of silver.[4] Platinum can be separated from gold by cupelling the cornet with about 12 times its weight of silver and parting with hot nitric acid (sp. gr. 1·42).[5] The residual gold is washed, dried and weighed.[6] The operations are repeated until the residual gold has a constant weight, showing that all the platinum has been removed.[7]

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[1] P. Petrenko-Kritschenko, *Zeit. anorg. Chem.*, **4**, 247, 1893; U. Antony, *Gazz. Chim. Ital.*, **23**, i, 184, 1893.

[2] C. E. Claus, *Liebig's Ann.*, **59**, 234, 1846; *Journ. prakt. Chem.*, (1), **39**, 88, 1846; *Journ. pharm.*, **11**, 76, 137, 1847; L. R. von Fellenberg, *Pogg. Ann.*, **50**, 61, 1840; U. Antony and A. Lucchesi, *Gazz. Chim. Ital.*, **29**, ii, 312, 1899; **30**, ii, 539, 1900.

[3] In cupelling alloys of platinum, gold, silver and lead, the greater the proportion of platinum the higher the temperature required for the cupellation. Alloys with over 50 per cent. of platinum cannot be freed from lead except at the temperature of the oxyhydrogen flame. C. O. Bannister and G. Patchin, *Inst. Min. Met.*, **23**, 163, 1913; J. Loevy, *Chem. Ztg.*, **38**, 82, 1914; J. F. Thompson and E. H. Miller, *Journ. Amer. Chem. Soc.*, **28**, 1115, 1906. For iridium, C. O. Bannister and E. A. du Vergier, *Analyst*, **39**, 340, 1914; A. F. Crosse, *Journ. Chem. Met. Min. Soc. S. Africa*, **14**, 373, 422, 483, 1914. For platinum in litharge, F. Michel, *Chem. Ztg.*, **39**, 6, 1915.

[4] C. Winkler, *Zeit. anal. Chem.*, **13**, 369, 1874; P. Oehmichen, *Berg. Hütt. Ztg.*, **60**, 137, 1901; M. Trenkner, *Met.*, **9**, 103, 1912; *Min. Eng. World*, **37**, 342, 1912; F. P. Dewey, *Journ. Ind. Eng. Chem.*, **6**, 650, 728, 1914.

[5] J. Spiller (*Proc. Chem. Soc.*, **18**, 118, 1897) states that nitric acid (sp. gr. 1·42) will dissolve 0·75 to 1·25 per cent. of platinum along with silver; while a weaker acid (sp. gr. 1·2) will dissolve only 0·25 per cent. of platinum; and a stronger acid will lead to the separation of platinum black. E. Priwoznik, *Berg. Hütt. Ztg.*, **44**, 325, 1895; H. Carmichael, *Journ. Soc. Chem. Ind.*, **22**, 1324, 1903.

[6] If the gold be very finely divided, it is best to filter and wash, so that the fine particles of gold will not contaminate the silver solution.

[7] If palladium be present, it will dissolve with the silver; while if iridium be present, it will remain with the gold. E. H. Miller, *School Mines Quart.*, **17**, 26, 1896; H. R. Jolley, *Journ. Chem. Met. Min. Soc. S. Africa*, **15**, 51, 1915.

The silver solution is largely diluted with water or, better, evaporated to drive off the excess of acid and then treated with a dilute solution of hydrogen sulphide. The silver sulphide which separates carries down the platinum as well.[1] Let the mixture stand overnight. Filter and wash in a porcelain dish. Dry the precipitate and ignite it with the filter-paper at a low temperature. Wrap the residue in a small piece of "assay lead-foil," and cupel. The resulting bead is parted with concentrated sulphuric acid, when the platinum remains behind as a dark spongy mass. The sponge is again boiled with fresh acid, washed by decantation, dried and weighed as platinum.[2]

The first cupellation enables the gold, silver and platinum to be determined; the result of the nitric acid parting gives the gold; and the sulphuric acid parting, the platinum; the silver is obtained by difference.

The Separation of Platinum by Potassium or Ammonium Chloride.— Platinum can be separated from solutions containing the copper and aluminium groups [3] by almost neutralising the acid solution with ammonia, evaporating the solution to the crystallisation point and adding water in just sufficient quantity to dissolve the crystals. Then add an excess of a saturated solution of potassium chloride to the feebly acid solution, and, after well mixing, add an excess of alcohol. Cover the vessel with a clock-glass and let the mixture stand in a warm place for about 24 hours. Collect the precipitate on an asbestos-packed Gooch crucible, and wash the precipitated potassium platinichloride, K_2PtCl_6, with 80 per cent. alcohol, as indicated for the determination of potassium (page 231). The potassium chloroplatinate can be dried and weighed; or reduced to metal and the metal weighed. Ammonium chloride is preferable to potassium chloride as precipitant, because the resulting ammonium chloroplatinate, $(NH_4)_2PtCl_6$, can be washed with a saturated solution of ammonium chloride and ignited—very gently at first to avoid the risk of loss by spurting. Furthermore, ammonium chloroplatinate is appreciably less soluble than the corresponding potassium salt. The metallic platinum which remains behind can be weighed directly. If iridium be present in the solution, it may also be precipitated with the ammonium chloroplatinate, to which it imparts a reddish tinge.[4] If the ignited mass be digested with

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[1] F. P. Dewey, *Journ. Ind. Eng. Chem.*, 4, 257, 1912; *Min. Eng. World*, 36, 503, 1912. Traces of gold in the solution of silver could also be gathered with the silver in a similar way.

[2] To make sure the residue is platinum, dissolve it in a few drops of aqua regia, evaporate the solution to drive off the excess of acid, and test it qualitatively with potassium iodide, or ammonium chloride. If palladium was present in the original sample it will be found in the acid solution after parting. According to A. C. Dart (*Met. Chem. Eng.*, 9, 75, 1911; 10, 219, 1912), the silver can be precipitated as chloride and the palladium precipitated as metal by boiling the filtrate, made ammoniacal with ammonia and acidified with formic acid. The silver chloride, it may be added, is very liable to carry down traces of other metals. If iridium be associated with the gold, the latter can be removed by digesting the mixture at 40° with a mixture of nitric acid (sp. gr. 1·34) with three times its volume of hydrochloric acid, and all diluted with five times its volume of water. The washed and dried residue is iridium. The difference in the two weighings represents the gold. See C. Toombs, *Journ. Chem. Met. Min. Soc. S. Africa*, 14, 4, 1914; J. Gray, *ib.*, 14, 2, 1914; M. van Brenkeleveen, *Rec. Trav. chim.*, 36, 285, 1917.

[3] Metals precipitated by soluble chlorides—silver, lead and mercurous salts—are assumed to be absent.

[4] For the solubilities of ammonium platinichloride and ammonium iridichloride in water and ammonium chloride solutions, see E. H. Archibald and J. W. Kern, *Trans. Roy. Soc. Canada*, 11, (iii), 7, 1918. Even in concentrated ammonium chloride solution, the solubility of the iridichloride is several times that of the platinum salt and advantage can be taken of this difference in solubility to effect the complete separation of iridium and platinum. For the separation of palladium and platinum, see P. Cohn and F. Fleissner, *Monats.*, 17, 361, 1896.

dilute aqua regia (1 : 5) [1] at 40°, the platinum dissolves and metallic iridium remains as an insoluble black powder. This is washed, dried and weighed.

General Analysis of the Platinum Metals.[2]—It is not often that an analysis of this kind is needed.[3] The sample is treated with concentrated aquá regia at 70° until there is no further perceptible action.[4] The liquid is diluted somewhat with warm water and the insoluble residue—probably osmiridium—filtered off. Fuse one part by weight of sodium hydroxide in a capacious nickel crucible and add gradually an intimate mixture of one part of the insoluble residue with four parts of sodium peroxide.[5] Keep the mass in a semi-fluid condition for about half an hour and stir frequently with a nickel spatula. Dissolve the cold mass in dilute hydrochloric acid and add the liquid to the main solution. The acid solution may contain salts of gold, osmium, rhodium, platinum, palladium, ruthenium, iridium, along with chromium, manganese, iron, etc., and nickel from the crucible.[6]

1. *Removal of Osmium and Ruthenium.*[7]—If the solution contains osmium and ruthenium, they are removed at this stage by distillation as the tetroxides. For this purpose a 700 c.c. distillation flask is connected to a train of three 300 c.c. absorption flasks, as shown in fig. 106.[8] Owing to the ease with which osmium tetroxide is reduced to the dioxide, it is essential to avoid contact either with rubber or any organic lubricant.

[1] Iridium is soluble when heated with concentrated aqua regia. "Iridium grey" and "platinum grey" colours can be analysed by these processes. For the determination of iridium in platinum-iridium alloys, see C. O. Bannister and E. A. du Vergier, *Analyst*, **39**, 340, 1914.

[2] L. E. Rivot, *Docimasie*, Paris, **4**, 1103, 1866; R. Jagnaux, *Analyse Chimique des Substances Commerciales, Minérales et Organiques*, Liège, 1888; W. Crookes, *Select Methods in Chemical Analysis*, London, 437–477, 1905; H. St C. Deville and H. Debray, *Ann. Chim. Phys.*, (5), **56**, 439, 1859; R. W. Bunsen, *Liebig's Ann.*, **146**, 265, 1868; C. Claus, *Beiträge zur Chemie der Platinmetalle*, Dorpat, 1854; M. C. Lea, *Chem. News*, **10**, 279, 301, 1864; **11**, 3, 13, 1865; *Amer. J. Science*, (2), **38**, 81, 248, 1864; W. Gibbs, *ib.*, (2) **31**, 63, 1861; (2), **34**, 353, 1862; E. Leidié, *Compt. rend.*, **131**, 888, 1901; *Bull. Soc. chim.*, (3), **25**, 9, 1901; **27**, 179, 1902; F. Mylius and F. Förster, *Ber.*, **25**, 665, 1892; H. Arnold, *Zeit. anal. Chem.*, **51**, 550, 1912; E. V. Koukline, *Rev. Met.*, **9**, 815, 1912; T. Wilm, *Ber.*, **18**, 2536, 1885; H. St C. Deville and J. S. Stas, *Procès Verbaux Comité Poids Mesures*, 153, 1877; F. Mylius and R. Dietz, *Ber.*, **31**, 3191, 1898; E. Leidié and L. Quennessen, *Bull. Soc. chim.*, (3), **25**, 840, 1901; *Chem. News*, **84**, 216, 1901; M. Wunder and V. Thuringer, *Zeit. anal. Chem.*, **52**, 740, 1913; F. Mylius and A. Mazzucchelli, *Zeit. anorg. Chem.*, **89**, 1, 1914; M. Schwitter, *Eng. Min. Journ.*, **97**, 1249, 1914; L. Quennessen, *Ind. Chim. Rev. Prod. chim.*, **5**, 6, 1918; A. T. Grigoriev *et al.*, *Ann. Inst. Platine*, **4**, 343, 1926; S. F. Shemtschushni (Zhemchuzhnii), *ib.*, **5**, 364, 1927; S. C. Ogburn, junr., *Journ. Amer. Chem. Soc.*, **48**, 2493, 1926; *Chem. Eng. Min. Rev.*, **20**, 142, 170, 1928; W. Graulich, *Oester. Chem. Ztg.*, **33**, 2, 1930; W. R. Schoeller, *Analyst*, **55**, 550, 1930; Anon., *Ann. Inst. Platine*, **9**, 109, 1932; B. G. Karpov *et al.*, *ib.*, **9**, 91, 93, 96, 99, 1932; B. G. Karpov and A. N. Fedorova, *ib.*, **12**, 163, 1935.

[3] Some difficulties in the manufacture of "platinum lustres" have been attributed to the presence of elements of this group other than platinum.

[4] If osmium and ruthenium be present in the soluble portion, which is not likely, the operation must be conducted in a flask fitted with a reflux condenser.

[5] For the separate analysis of the first insoluble residue obtained on dissolving platinum ore in aqua regia, see S. F. Shemtschushni (Zhemchuzhnii) *et al.*, *Ann. Inst. Platine*, **4**, 355, 1926; B. G. Karpov *et al.*, *ib.*, **9**, 102, 1932.

[6] E. Leidié and L. Quennessen, *Bull. Soc. chim.*, (3), **25**, 840, 1901; (3), **27**, 179, 1902.

[7] A. Joly, *Encyc. Chim. de Fremy*, Paris, **3**, 236, 1892; C. E. Claus, *Bull. St Petersburg Acad. Sci.*, **1**, 97, 1860; J. L. Howe and F. N. Mercer, *Journ. Amer. Chem. Soc.*, **47**, 2926, 1925; J. L. Howe, *ib.*, **49**, 2393, 1927; S. F. Shemtschushni (Zhemchuzhnii) *et al.*, *Ann. Inst. Platine*, **4**, 355, 1926; B. G. Karpov *et al.*, *ib.*, **9**, 102, 1932; S. Saito, *Bull. Inst. Phys. Chem. Res. Tokyo*, **8**, 164, 1929; E. Fritzmann, *Zeit. anorg. Chem.*, **163**, 165, 1927; **169**, 356, 1928. For the separation of ruthenium from the platinum metals, other than osmium, see R. Gilchrist, *Bur. Standards Journ. Research*, **12**, 283, 1934.

[8] This is the type of apparatus recommended by R. Gilchrist, *Bur. Standards Journ. Research*, **6**, 421, 1931; J. J. Russell, F. E. Beamish and J. Seath, *Ind. Eng. Chem. Anal. Ed.*, **9**, 475, 1937.

Hence an all-glass apparatus with accurately ground glass joints, sealed only by a thin film of water, must be used. However, it is necessary to lubricate the stopcock of the thistle funnel in the distillation flask with grease, but access of osmium tetroxide to it is prevented by constricting the delivery tube so that it holds a column of water. During the distillation, this tube is frequently flushed out with liquid. The thistle funnel between the first two absorption flasks serves to introduce, if necessary, further quantities of the absorbing solution and also to rinse out the connecting tube. The first absorption flask is charged with 150 c.c. of hydrochloric acid (sp. gr. 1·1) and the other two flasks with 50 c.c. each of the same solution. The solution under investigation is poured into the distilling flask and an excess of sodium hydroxide is added through the thistle funnel, after which a slow current of chlorine [1] is bubbled through the liquid. When the liquid
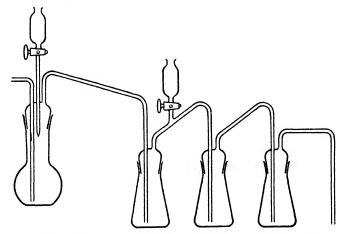
Fig. 106.—Separation of Osmium and Ruthenium from the Other "Platinum Metals."

in the flask is saturated with chlorine, raise the temperature to 70°–80°, when the ruthenium tetroxide and part of the osmium tetroxide will distil over. Finally raise the temperature to the boiling-point to eliminate all the osmium. The distillation will take about an hour, more or less, depending on the amount of osmium and ruthenium present. The liquid in the distilling flask must be kept alkaline [2] otherwise the ruthenium will be incompletely volatilised.[3] When all the ruthenium and osmium have volatilised,[4] the current of chlorine is stopped and the apparatus cooled. The ruthenium tetroxide in the condensing flask forms a stable trichloride, $RuCl_3$, while the osmium tetroxide undergoes no change.

2. *The Separation of Ruthenium and Osmium.*—The liquid from the absorption flasks is saturated with sulphur dioxide to reduce the osmium tetroxide to the non-volatile dioxide and then evaporated down, with the sulphur dioxide still running, until the hydrochloric acid has been removed. The solution is next diluted to a volume of about 100 c.c. and transferred to a clean distillation flask. According to Gilchrist, osmium can be completely distilled from nitric acid solutions, but no ruthenium is eliminated from boiling solutions containing less than 40 per cent. by volume of nitric acid. Hence, following Gilchrist's procedure, charge the absorption flasks, as before, with hydrochloric acid (sp. gr. 1·1) which has been freshly saturated with sulphur dioxide. Add to the solution in the distillation flask 40 c.c. of nitric acid (1 : 1) through the thistle funnel and flush out the funnel and stopcock with 10 c.c. of water. Pass a slow current of air through the apparatus and heat the solution in the distillation flask to boiling. Continue

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[1] Say, from a cylinder of chlorine.

[2] If necessary, add more sodium hydroxide *via* the thistle funnel.

[3] E. Leidié and L. Quennessen, *Compt. rend.*, **136**, 1399, 1903.

[4] A drop of the distillate will give no blackening with hydrogen sulphide if the action is over.

the distillation for an hour. Cool down, empty and rinse out the absorption flasks, reserving the solution and washings for the determination of osmium. The solution in the distillation flask is now made alkaline with sodium hydroxide and the ruthenium in it distilled over in a current of chlorine into hydrochloric acid, as in the initial distillation.

3. *The Determination of Ruthenium and Osmium—Gilchrist's Process.*[1]—The liquid and washings from the absorption flasks, containing the ruthenium, are evaporated down to small bulk to remove the excess of hydrochloric acid, then diluted with water to about 150 c.c. and the solution heated to boiling. A saturated and filtered solution of sodium bicarbonate is added until the precipitate of hydrated ruthenium dioxide coagulates. A few drops of bromocresol purple indicator are added and then sufficient sodium bicarbonate to produce a faint purple colour. After boiling for 5 minutes, the solution is filtered and the precipitate washed thoroughly with a hot 1 per cent. ammonium sulphate solution until free from chlorides. It is finally washed three or four times with a cold 2·5 per cent. solution of ammonium sulphate. The paper containing the precipitate is slowly charred in a porcelain crucible and the residue then ignited to burn off the carbon. The crucible is now covered with a Rose's lid and its contents are heated in a current of hydrogen. After the reduction is complete, the metallic ruthenium is cooled in hydrogen and weighed as such. The solution and washings containing the osmium are evaporated down to small bulk on a water bath. The residue is digested with hydrochloric acid (sp. gr. 1·18) for 15 minutes and evaporated a second time. The digestion with acid and subsequent evaporation are repeated, in all, three times more in order to decompose completely any sulphite compounds of osmium. The final residue is diluted to 150 c.c. and the solution precipitated with sodium bicarbonate exactly as for ruthenium. A few drops of bromophenol blue indicator are now added to the solution and the addition of sodium bicarbonate continued until a faint bluish colour is given. The supernatant liquid is first filtered through a Munroe's crucible[2] (page 93) and the precipitate then transferred to the crucible. The precipitate is washed thoroughly with a hot 1 per cent. solution of ammonium chloride, followed by a cold saturated solution until, on continuing the suction, the bottom of the crucible is coated with the solid salt. After wiping off this coating, the bottom of the crucible is covered with a platinum cap to prevent subsequent access of air. A small jet of burning hydrogen is now introduced into the crucible through a silica Rose's crucible tube and lid so that it burns from underneath the edge of the lid. After 5 minutes, the crucible is gradually heated to volatilise the ammonium chloride and then strongly for 10 minutes. After cooling the crucible by removing the burner, the hydrogen flame is extinguished and the crucible cooled to room temperature in hydrogen. The hydrogen is finally replaced by a current of carbon dioxide and the crucible weighed. Great care must be taken to exclude air during the ignition, otherwise volatile osmium tetroxide will be formed.

4. *The Separation of Iridium.*[3]—The liquid remaining in the distillation flask, after the removal of the osmium and ruthenium, is boiled to expel free chlorine and then acidified with hydrochloric acid to dissolve the suspended hydroxides. The solution is filtered to remove silica, which may have been formed by the action of the hot sodium hydroxide solution on the walls of the flask. To the solution add a moderate excess of ammonium chloride and two-thirds its volume of alcohol. Let the mixture stand about 24 hours. The

[1] R. Gilchrist, *Bur. Stand. Journ. Research*, 3, 993, 1930; 6, 421, 1931. Compare B. G Karpov, S. E. Krasikov and A. N. Fedorova, *Ann. Inst. Platine*, 12, 159, 1935.

[2] Filter-paper is inadmissible, since on ignition the osmium will be oxidised to the volatile tetroxide. A thickly packed Gooch crucible may be used, but air is liable to diffuse through its base and attack the osmium.

[3] For the separation of iridium, see U. Antony, *Gazz. Chim. Ital.*, 22, (1), 275, 1892; C. O. Bannister and E. A. du Vergier, *Analyst*, 39, 340, 1914; R. Gilchrist, *Journ. Amer. Chem. Soc.*, 45, 2820, 1923; S. Aoyama, *Zeit. anorg. Chem.*, 133, 230, 1924; W. R. Schoeller, *Analyst*, 51, 392, 1926; O. E. Zvjagintsev, *Ann. Inst. Platine*, 5, 189, 1927; B. G. Karpov, *ib.*, 4, 360, 1926; B. G. Karpov and A. N. Fedorova, *ib.*, 9, 106, 1932; 11, 135, 1933; L. Moser and H. Hackhofer, *Monats*, 59, 44, 1932.

precipitate contains most of the iridium and platinum, with traces of palladium and rhodium.   Filter and wash the precipitate a few times with half-saturated ammonium chloride solution, containing a drop of hydrochloric acid.   The filtrate, after the addition of 1 c.c. of conc. nitric acid, is evaporated on a water bath almost to crystallisation point, and the solid which separates, if any, is filtered off and washed as before with ammonium chloride solution.   The filtrate (filtrate A) is retained.   The two precipitates are transferred to a weighed porcelain crucible, dried and the ammonium chloride fumed off at as low a temperature as possible.   When all volatile matter has been expelled, the filter-paper is burnt off and the residue finally reduced at a red heat in a current of hydrogen.   The metal is now filtered off, washed thoroughly with hot water to remove traces of mineral salts, again ignited and reduced in the same crucible as before.   The reduced metals are digested with aqua regia ($1HNO_3$, $3HCl$, $3H_2O$).   The platinum and any co-precipitated palladium pass into solution, the iridium and traces of rhodium, if any, remain undissolved. Filter and wash.   After calcination, the insoluble residue is carefully fused with potassium bisulphate, avoiding loss by spurting (page 166).   Any rhodium forms a soluble salt which subsequently passes into solution; the iridium is oxidised but it does not dissolve.   The cold cake is digested in dilute sulphuric acid and, after filtering and washing free from sulphates, the insoluble residue is calcined in the weighed porcelain crucible, reduced in hydrogen and weighed as *iridium*.[1]   The filtrate (filtrate B) is reserved for the determination of rhodium.

5. *The Separation of Platinum.*—The dilute aqua regia solution, containing the platinum, with possibly traces of palladium, is repeatedly evaporated with excess of hydrochloric acid to remove nitric acid.   The residue is moistened with hydrochloric acid, taken up in water and zinc added to the solution. Platinum and palladium are precipitated.   Filter and wash with water, acidified with hydrochloric acid.   Ignite and weigh as *platinum*.[2]

6. *The Separation of Palladium.*—Combine filtrates A and B, boil gently to expel the alcohol and nearly neutralise the excess of acid.   Cool and saturate the cold, weakly acid solution with hydrogen sulphide.   Gold, copper and palladium are quantitatively precipitated, with possibly some rhodium, if present in considerable quantity.   Filter and wash the precipitated sulphides. Strongly acidify the filtrate with hydrochloric acid and pass hydrogen sulphide through the hot solution.   All the rhodium in the solution is precipitated.[3] Filter and wash as before.   The filtrate from the sulphide precipitations contains the metals of the iron-aluminium group, together with the nickel from the crucible used in the initial fusion [4] (see page 265).   The two sulphide

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[1] This may still contain a trace of rhodium and possibly of iron.   For the separation of iridium and rhodium, see Claus (*l.c.*); Deville and Debray (*l.c.*); I. Wada and T. Nakazono, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, **1**, 139, 1923; V. V. Lebedinski, *Ann. Inst. Platine*, **5**, 364, 1927; B. G. Karpov, *ib.*, **6**, 98, 1928; **9**, 108, 1932; R. Gilchrist, *Bur. Stand. Journ. Research*, **9**, 547, 1932; *ib.*, **12**, 283, 291, 1934.   For the separation of iridium and iron, see Moser and Hackhofer (*l.c.*); Schoeller (*l.c.*).

[2] The residue may contain palladium and perhaps traces of iridium.   For the separation of palladium and platinum, see H. D. Greenwood, *Chem. Zentr.*, (1), 220, 1915; A. M. Smoot, *ib.*, (1), 220, 1915; *Öster. Zeit. Berg. Hüttenw.*, **62**, 578, 1914; W. Schmidt, *Zeit. anorg. Chem.*, **80**, 335, 1913; W. Manchot, *Ber.*, **58B**, 2518, 1925; J. Hanuš, A. Jílek and J. Lukas, *Chem. News*, **131**, 401, 1925; **132**, 1, 1926; S. C. Ogburn, junr., and A. H. Reismayer, *Journ. Amer. Chem. Soc.*, **50**, 3018, 1928; S. C. Ogburn, junr., and W. C. Brastow, *ib.*, **55**, 1307, 1933; O. E. Zvjaginstev, *Ann. Inst. Platine*, **4**, 364, 1926.

[3] I. Wada and S. Saito, *Bull. Inst. Phys. Chem. Res. Tokyo*, **8**, 749, 1929.

[4] Note, nickel usually contains a small proportion of iron.   Hence, if iron is to be determined, the iron content of the nickel crucible must be known and an allowance made from the loss in weight of the crucible after the peroxide fusion—Schoeller (*l.c.*).

precipitates are roasted and the residue digested with hydrochloric acid; palladium and copper pass into solution, gold and rhodium remain undissolved. Filter, wash and neutralise the cold filtrate with 1·0N-sodium carbonate solution until alkaline to phenolphthalein, then add 0·2 c.c. in excess. Copper, if present, will be precipitated. Stand for 30 minutes, filter and wash the precipitate, if any. To the filtrate add an excess of a *cold* 1 per cent. alcoholic solution of dimethylglyoxime [1] and stand for 3 to 12 hours, depending on the amount of palladium present. Filter, wash with hot water, dry, ignite cautiously first in air, then in hydrogen, and weigh as *palladium*.

7. *The Separation of Rhodium and Gold.*—The insoluble residue of rhodium and gold, obtained in the palladium separation, is digested with aqua regia. The gold dissolves and the rhodium remains insoluble. Filter and wash. Precipitate the *gold* from the filtrate in the usual manner; dry and weigh the insoluble powder as metallic *rhodium*.[2]

The above method gives a very fair approximation. The results check very fairly against more elaborate schemes.[3]

§ 236. The Detection of Selenium.

Selenium and tellurium determinations [4] are very rarely needed in technical analyses for the silicate industries. Selenium is used in the preparation of certain reddish colours, and in bleaching and decolorising glasses and special enamel frits.[5] In the latter case, the amount in question may vary from 0·002 to 0·004 per cent., and a qualitative test [6] may then reveal whether or not selenium is present; but quantitative determinations are only satisfactory if a relatively large amount of the material is taken for the analysis.

In the regular course of qualitative analysis, selenium [7] and tellurium appear as members of the sub-group of elements whose sulphides are precipitated by hydrogen sulphide in acid solutions, and whose sulphides are also

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[1] For the glyoxime process for palladium, see M. Wunder and V. Thuringer, *Zeit. anal. Chem.*, 52, 101, 660, 1913; A. Gutbier and C. Fellner, *ib.*, 54, 205, 1915; F. Krauss and H. Deneke, *ib.*, 67, 86, 1925; C. W. Davis, *U.S. Bur. Mines Repts. Investigations*, No. 2351, 1922; *ib.*, No. 2731, 1926; H. E. Zschiegner, *Ind. Eng. Chem.*, 17, 294, 1925; S. C. Ogburn, junr., *Journ. Amer. Chem. Soc.*, 48, 2507, 1926; *Chem. Eng. Min. Rev.*, 20, 142, 170, 1928; W. Graulich, *Oester. Chem. Ztg.*, 33, 2, 1930; Anon., *Ann. Inst. Platine*, 9, 109, 1932; B. G. Karpov, *ib.*, 9, 108, 1932; H. Holzer, *Zeit. anal. Chem.*, 95, 392, 1933; F. E. Beamish and M. Scott, *Ind. Eng. Chem. Anal. Ed.*, 9, 460, 1937. For alternative methods of separation, see footnote 2, p. 479. For the colorimetric determination of palladium, see A. A. Christman and E. L. Randall, *Journ. Biol. Chem.*, 102, 595, 1933; A. A. Christman, W. D. Black and J. Schultz, *Ind. Eng. Chem. Anal. Ed.*, 9, 153, 1937.

[2] It will be observed that traces of the platinum metals which escape precipitation accumulate with the gold and rhodium. For the separation of rhodium, see also E. Wichers, *Journ. Amer. Chem. Soc.*, 46, 1818, 1924; L. Moser and H. Gruber, *Monats.*, 59, 61, 1932; O. E. Zvjaginstev, *Journ. App. Chem. (U.S.S.R.)*, 5, 217, 1932.

[3] For reviews of recent analytical methods for determining the platinum metals, see M. Frommes, *Zeit. anal. Chem.*, 99, 305, 1934; R. Gilchrist and E. Wichers, *IX Cong. Intern. Quim. Pura Applicata* (Madrid), 6, 32, (1934), pub. 1936; *Journ. Amer. Chem. Soc.*, 57, 2565, 1935.

[4] Tellurium determinations are chiefly required in the analysis of cupriferous pyrites and auriferous ores for metallurgical purposes.

[5] F. Kraze, *Sprechsaal*, 45, 214, 227, 1912; P. Fenaroli, *Chem. Ztg.*, 36, 1149, 1912; 38, 117, 1914; W. D. Treadwell, *Ker. Rund.*, 20, 220, 1912; O. N. Witt, *ib.*, 22, 293, 1914.

[6] For the detection of selenium in glass by codeine sulphate, see E. J. C. Bowmaker and J. D. Cauwood, *Journ. Soc. Glass Tech.*, 11, 386, 1927.

[7] A. Gutbier and J. Lohmann, *Zeit. anorg. Chem.*, 42, 325, 1904; 43, 384, 1905; A. Bettendorf and G. von Rath, *Pogg. Ann.*, 139, 329, 1870; W. Muthmann, *Zeit. Krist.*, 17, 357, 1890; W. E. Ringer, *Zeit. anorg. Chem.*, 32, 183, 1902; E. von Gerichten, *Ber.*, 7, 26, 1874; A. Ditte, *Compt. rend.*, 73, 625, 660, 1871.

soluble in sodium monosulphide.   When hydrogen sulphide is passed through a slightly acid solution of tellurous acid or a salt, a dark reddish-brown precipitate is given which soon becomes almost black.   Analysis of the precipitate shows that it contains tellurium and sulphur in the proportions required for TeS_2, and this led Berzelius [1] to assume that the precipitate was a true sulphide. Becker showed that carbon disulphide dissolved out the sulphur, and hence he assumed that the supposed sulphide is but a mixture of sulphur and tellurium, formed by reduction of the tellurous acid: $2H_2S + H_2TeO_3 = Te + 2S + 3H_2O$. At low temperatures, however, a sulphide, TeS, is formed, but it rapidly decomposes at temperatures above $0°$.   If selenium sulphide be precipitated from a cold solution, the lemon-yellow selenium sulphide—SeS_2—is readily dissolved by alkali sulphides.   If the solution be hot, the precipitate is orange-yellow and is much less soluble.   Though hydrogen sulphide separates selenium from the elements which do not give precipitates with hydrogen sulphide in acid solutions, *selenium sulphide [2] cannot be quantitatively separated from the mixed sulphides of the hydrogen sulphide group by the action of sodium or ammonium sulphide.*   Part of the selenium passes into solution and part remains associated with the insoluble sulphides.   In fact, from two-thirds to seven-eighths of the total selenium may remain with the insoluble sulphides of copper, bismuth and lead.   For example, a solution of copper and selenium in dilute hydrochloric acid, just acid enough to prevent the precipitation of copper selenide, was treated [3] with hydrogen sulphide.   The precipitate was digested with concentrated sodium monosulphide, washed with water containing a little sodium sulphide and a little hydrogen sulphide, and finally with strong alcohol.   The insoluble part, in four experiments, contained:

Sulphur	.	. 0·3787	0·1649	0·1730	0·0416 grm.
Selenium	.	. 0·2828	0·1726	0·1565	0·0239 grm.
Copper	.	. 0·9880	0·4880	0·4909	0·0979 grm.

Hence the alkali sulphide effects a very imperfect separation when selenium and copper are together precipitated in an acid solution.   The process, however, is used in qualitative analysis.

The selenium is precipitated from the ammonium or sodium sulphide solution by treatment with acids.[4]   The washed and dried precipitate is mixed with twice its weight of a flux made by mixing equal parts of sodium nitrite and sodium carbonate.   The mixture is added to a crucible containing two parts by weight of previously fused sodium nitrite.   The mixture is fused up and poured while molten on a porcelain slab, and the cold mass and also the residue in the crucible, if any, are extracted with water—sodium antimonate, stannic oxide (gold, platinum and iridium) remain insoluble; selenic (telluric),

[1] J. J. Berzelius, *Ann. Chim. Phys.*, (2), **32**, 411, 1826; Fr. Becker, *Liebig's Ann.*, **180**, 257, 1876; B. Brauner, *Journ. Chem. Soc.*, **57**, 527, 1895; A. Gutbier, *Studien über das Tellur*, Leipzig, 51, 1901; W. O. Snelling, *Journ. Amer. Chem. Soc.*, **34**, 802, 1912; A. Gutbier and F. Flury, *Zeit. anorg. Chem.*, **32**, 272, 1902.
[2] According to B. Rathke (*Liebig's Ann.*, **152**, 181, 1869; *Ber.*, **18**, 1534, 1885; **36**, 594, 1903), the precipitate is a mixture of SeS_2, Se_2S, and S.   Some hold that the precipitate from selenious acid is a mixture of selenium and sulphur.   H. Rose, *Pogg. Ann.*, **107**, 186, 1859; **113**, 473, 1861; E. Divers and M. Shimosé, *Chem. News*, **51**, 199, 1885; E. Divers and T. Shmidzu, *Journ. Chem. Soc.*, **47**, 441, 1885; J. Meunier, *Ann. Chim. Ital.*, **22**, 41, 1917.
[3] E. Keller, *Journ. Amer. Chem. Soc.*, **19**, 771, 778, 1897; **22**, 241, 1900; J. Meyer and J. Jannek, *Zeit. anal. Chem.*, **52**, 534, 1913.
[4] The ammonium or sodium sulphide solution contains selenium, molybdenum, tin, antimony, arsenic, tellurium, gold, platinum, etc.

molybdic and arsenic acids are dissolved as sodium salts.   Add an excess of hydrochloric acid and boil the solution to reduce the sodium selenate, Na_2SeO_4, to selenious acid, H_2SeO_3:

$$Na_2SeO_4 + 4HCl = 2NaCl + H_2SeO_3 + H_2O + Cl_2$$

Then boil the solution with sulphurous acid,[1] a hydrazine salt[2]—sulphate, hydrochloride or hydrate—hydroxylamine,[3] or some other suitable reducing agent.[4]   Brown or red-coloured selenium is precipitated.[5]

For opening glasses and frits, treat 5 grms. of the finely powdered material

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[1] H. Rose, *Pogg. Ann.*, 113, 472, 1861; *Zeit. anal. Chem.*, 1, 73, 1862; A. Angeletti, *Gazz. Chim. Ital.*, 53, (1), 339, 1923; V. Lenher and D. P. Smith, *Ind. Eng. Chem.*, 16, 837, 1924; V. Lenher and C. H. Kao, *Journ. Amer. Chem. Soc.*, 47, 769, 2454, 1925; E. H. Shaw and E. E. Reid, *ib.*, 49, 2330, 1927; E. Keller, *ib.*, 22, 241, 1900; E. T. Erickson, *Journ. Wash. Acad. Sci.*, 19, 319, 1929; K. Wagermann and H. Triebel, *Metall und Erz*, 27, 231, 1930; *Chem. Zentr.*, (2), 273, 1930; W. Geilmann and Fr. W. Wrigge, *Zeit. anorg. allgem. Chem.*, 210, 357, 1933; K. Brückner, *Zeit. anal. Chem.*, 94, 305, 1933; J. B. Krak, *Glass Ind.*, 9, 152, 1928; A. A. Borkovskii and A. A. Babalova, *Zavodskaya Lab.*, 3, 306, 1934.

[2] P. Jannasch and M. Müller, *Ber.*, 31, 2388, 1898; G. Pellini, *Gazz. Chim. Ital.*, 33, (1), 515, 1903; A. Gutbier, G. Metzner and J. Lohmann, *Zeit. anorg. Chem.*, 41, 291, 1904; J. Meyer and J. Jannek, *ib.*, 83, 51, 1913; J. Meyer, *Zeit. anal. Chem.*, 53, 145, 1914; A. Gutbier and F. Engeroff, *ib.*, 54, 193, 1915; V. Lenher and C. H. Kao, *Journ. Amer. Chem. Soc.*, 47, 2454, 1925; E. Benesch and E. Erdheim, *Chem. Ztg.*, 54, 954, 1930; K. Wagermann and H. Triebel, *Metall und Erz*, 27, 231, 1930; *Chem. Zentr.*, (2), 273, 1930; V. Hovorka, *Coll. Czech. Chem. Comm.*, 4, 300, 1932; K. Brückner, *Zeit. anal. Chem.*, 94, 305, 1933; A. Cousen, *Journ. Soc. Glass Tech.*, 7, 303, 1923.

[3] P. Jannasch and M. Müller, *Ber.*, 31, 2388, 2393, 1898; A. Gutbier, *Ber.*, 34, 2724, 1901; *Studien über das Tellur*, Leipzig, 65, 1901; *Liebig's Ann.*, 320, 52, 1902; *Zeit. anorg. Chem.*, 29, 22, 1902; 31, 331, 340, 1902; 32, 31, 51, 91, 96, 108, 260, 272, 1902; V. Lenher and C. H. Kao, *Journ. Amer. Chem. Soc.*, 47, 2454, 1925; R. Rosenheim and M. Weinheber, *Zeit. anorg. Chem.*, 69, 266, 1911.   For tellurium it is recommended that the reduction be effected in a weakly alkaline solution with a 10 per cent. solution of hydrazine sulphate contained in a beaker placed in an autoclave heated to 130° under a pressure of 3 or 4 atmospheres.   See also V. Lenher and A. W. Homberger, *Journ. Amer. Chem. Soc.*, 30, 387, 1908; V. Lenher and C. H. Kao, *ib.*, 47, 769, 2454, 1925; J. B. Menke, *Zeit. anorg. Chem.*, 77, 282, 1912; V. Lenher and D. P. Smith, *Ind. Eng. Chem.*, 16, 837, 1924; K. Wagermann and H. Triebel, *Metall und Erz*, 27, 231, 1930; *Chem. Zentr.*, (2), 273, 1930; O. E. Clauder, *Zeit. anal. Chem.*, 89, 270, 1932; W. Geilmann and Fr. W. Wrigge, *Zeit. anorg. allgem. Chem.*, 210, 357, 1933.

[4] Phosphorous acid (H. Rose, *Handbuch der analytischen Chemie*, Braunschweig, 2, 441, 1871; A. Gutbier, *Zeit. anorg. Chem.*, 41, 448, 1904); potassium iodide and hydrochloric acid (A. W. Peirce, *Amer. J. Science*, (4), 1, 416, 1896; *Zeit. anorg. Chem.*, 12, 409, 1896; F. A. Gooch and W. G. Reynolds, *ib.*, 10, 248, 1895; *Amer. J. Science*, (3), 50, 249, 1895; F. A. Gooch and A. W. Peirce, *ib.*, (4), 1, 31, 1896; *Zeit. anorg. Chem.*, 11, 249, 1896; W. Muthmann and J. Schäfer, *Ber.*, 26, 1008, 1893)—the reduction is more rapid than with sulphur dioxide, and a second reduction of the filtrate is not necessary; glucose (F. Stolba, *Zeit. anal. Chem.*, 11, 437, 1872); magnesium or aluminium (L. Kastner, *ib.*, 14, 142, 1875); hypophosphorous acid (A. Gutbier and E. Rohn, *Zeit. anorg. Chem.*, 34, 448, 1903; A. Gutbier, *ib.*, 32, 295, 1902; *ib.*, 41, 448, 1904); stannous chloride (A. Grak and J. Petrén, *Svensk Kem. Tidskrift*, 24, 128, 1912; P. Klason and H. Mellquist, *Arkiv Kem. Min. Geol.*, 4, No. 34, 1, 1913; M. Schmidt, *Metall und Erz*, 22, 511, 1925; *Chem. Zentr.*, (1), 739, 1926; A. A. Borkovskii and A. A. Babalova, *Zavodskaya Lab.*, 3, 306, 1934); oxalic, formic, malonic or pyruvic acid (W. O. de Coninck and W. Chauvenet, *Ann. Chim. anal.*, 21, 114, 1916); thiocarbamide (P. Falciola, *Ann. Chim. appl.*, 17, 357, 1927); formaldehyde (E. Kheraskova and L. Veisburt, *Zeit. anal. Chem.*, 102, 353, 1935).   For a general criticism of reducing agents, see A. Gutbier, G. Metzner and J. Lohmann, *Zeit. anorg. Chem.*, 41, 291, 1904; K. Wagermann and H. Triebel, *Metall und Erz*, 27, 231, 1930.   Hydrazine salts and sulphurous acid are recommended.

[5] H. Rose (*Zeit. anal. Chem.*, 1, 73, 1862; *Pogg. Ann.*, 113, 472, 624, 1861; *Chem. News*, 5, 185, 1862) has shown that the presence of hydrochloric acid is an essential factor in the complete reduction of selenium salts.   J. Meunier, *Compt. rend.*, 163, 332, 1916.

with sulphuric[1] and hydrofluoric acids in the usual manner.[2] Evaporate the solution to dryness. Digest the residue with water and filter. Selenium can be precipitated from the filtrate by boiling with a reducing agent. The aqueous extract of the sodium carbonate fusion can also be acidified and treated in a similar way.

§ 237. The Gravimetric Determination of Selenium— Sulphurous Acid Process.

Mix the powdered substance with 6 parts by weight of sodium carbonate and 1 part of sodium nitrite in a nickel crucible.[3] Raise the temperature very gradually until the mass is fused. Extract the cold mass with water. Sodium selenate passes into solution.[4] Acidify the solution with hydrochloric acid and boil until chlorine [5] is no longer evolved—starch-iodide paper held in the steam will show this.[6] The boiling solution is saturated with sulphur dioxide.[7] Selenium is precipitated. The boiling is continued for about 15 minutes.[8]

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[1] Sulphuric acid sometimes contains traces of selenium—see footnote 2, p. 486.

[2] J. B. Krak (*Glass Ind.*, **9**, 152, 1928) uses a mixture of nitric and hydrofluoric acids and removes the excess of the latter by repeated evaporation with nitric acid. A. Cousen (*Journ. Soc. Glass Tech.*, **7**, 303, 1923) decomposes the glass in the cold with diluted hydrofluoric acid (5 : 3) and dissolves the residue of selenium in hydrochloric acid and chlorine water, prior to reduction.

[3] Platinum crucibles are attacked by certain selenides. The crucible must be selected according to the nature of the material under investigation and the constituents to be sought. For selenium only, a porcelain crucible can be used. A nickel crucible with sodium peroxide fusions may also be used. E. Benesch and E. Erdheim (*Chem. Ztg.*, **54**, 954, 1930) open up insoluble materials by sintering in a nickel crucible one part of the sample with three parts each of ferric oxide powder and potassium chlorate and four parts of sodium bicarbonate.

[4] If a soluble alkali selenate be in question, the fusion is not needed.

[5] If the solution contains nitric acid, this must be removed by repeated evaporation with concentrated hydrochloric acid (page 464).

[6] According to Rathke, no appreciable loss of selenium will occur if the solution contains sodium or potassium chloride (B. Rathke, *Liebig's Ann.*, **152**, 194, 206, 1869; *Journ. prakt. Chem.*, (1), **108**, 249, 1869; *Zeit. anal. Chem.*, **9**, 484, 1870). J. Meyer (*Zeit. anal. Chem.*, **53**, 145, 1914) maintains the contrary. J. Meyer (*l.c.*), V. Hovorka (*Coll. Czech. Chem. Comm.*, **4**, 300, 1932) and A. Gutbier and F. Engeroff (*Zeit. anal. Chem.*, **54**, 193, 1915) report the mechanical loss of selenium in the spray of evolved nitrogen when hydrazine is used for reduction. The latter say that some hydrogen selenide is also formed, but that its production is minimised in the presence of citric acid. V. Lenher and D. P. Smith (*Ind. Eng. Chem.*, **16**, 837, 1924; K. Wagermann and H. Triebel, *Metall und Erz*, **27**, 231, 1930; W. Geilmann and Fr. W. Wrigge, *Zeit. anorg. allgem. Chem.*, **210**, 357, 1933) recommend distillation from sulphuric acid solution in a stream of gaseous hydrochloric acid. Volatile selenium tetrachloride passes over. It is collected in water and the aqueous solution subsequently reduced with sulphur dioxide. A little tellurium also distils over (W. Geilmann and Fr. W. Wrigge, *l.c.*).

[7] Sodium or ammonium bisulphite may also be used (H. Bauer, *Ber.*, **48**, 507, 1915; A. Michaelis, *ib.*, **48**, 873, 1915).

[8] According to H. Rose (*l.c.*), solutions of selenious acid cannot be heated above 100° without appreciable loss of selenium by volatilisation. In the case of nitric acid solutions,.the removal of nitric acid by evaporation on a water bath as recommended by Rose (*l.c.*; E. Divers and M. Shimosé, *Journ. Chem. Soc.*, **47**, 439, 1885; P. Michaelis, *Ber.*, **30**, 2827, 1897; R. E. Lyons and F. L. Shinn, *Journ. Amer. Chem. Soc.*, **24**, 1087, 1902) leads to low results. Boiling under a reflux condenser with concentrated hydrochloric acid, in order to remove the nitric acid, is not successful even after boiling for 6 hours. Lyons and Shinn add a quarter as much silver or zinc nitrate as is sufficient to combine with the selenium. The selenite so formed is stable at 100°, and insoluble enough in cold water to enable the precipitate to be washed free from nitric acid and nitrates. Evaporate the mixture to dryness. Wash down the sides of the vessel with a little water; evaporate again. Treat the residue with 50 c.c. of dilute ammonia and evaporate the solution to dryness; again add ammonia and again evaporate to dryness. The $Ag_2SeO_3 . NH_3$ so formed (B. Boutzoureano, *Ann. Chim. Phys.*, (6), **18**, 289, 1889) is insoluble in water and stable at 100°. Add water twice and evaporate after each addition

The precipitate becomes more compact and easier to filter after boiling. The colour also changes from red to dark brown. The precipitation is somewhat slow and it is necessary to test the filtrate, or a little of the clear liquid, with more reducing agent—say ammonium bisulphite—to make sure that precipitation is complete. If not, add more reducing agent and repeat the sequence of operations.[1] Collect the brown precipitate on a Gooch crucible; wash with hot water,[2] then with alcohol and finally with ether. Dry the crucible between 100° and 105°, and weigh as selenium—Se.[3]

The following numbers represent the type of results which can be obtained with this process in the presence of a large excess of copper sulphate:

Se used .   0·0100   0·0100   0·0500   0·0500   0·0100   0·0100   grm.
Se found   0·0094   0·0096   0·0507   0·0496   0·0103   0·0094   grm.

Effect of the Acidity of the Solution on the Precipitation of Selenium and Tellurium by Sulphur Dioxide.— This method of precipitating selenium—
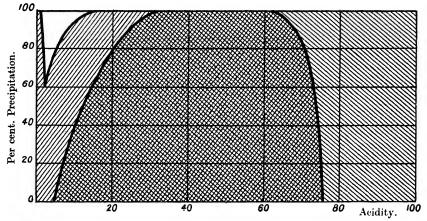
Fig. 107.—Influence of the Acidity of the Solution on the Precipitation of Selenium and Tellurium.

boiling with sulphur dioxide in the presence of hydrochloric acid—separates selenium from all metals not precipitated by sulphur dioxide, and also from arsenic, antimony and tin.[4] If much antimony be present, however, tartaric acid must be added to prevent the separation of antimony oxychloride, unless the solution be very strongly acid. The concentration of the hydrochloric acid

to drive off the ammonia. When cool, take up the residue with hydrochloric acid, filter, wash and reduce the selenium by sulphur dioxide. See also T. Gassmann, *Zeit. physiol. Chem.*, 100, 182, 1917.

[1] G. Pellini (*Gazz. Chim. Ital.*, 33, i., 515, 1903; G. Pellini and E. Spelta, *ib.*, 33, ii., 89, 1903) adds 50 to 100 c.c. of a saturated solution of ammonium tartrate and warms the solution for a couple of hours at 50° to 60° with hydrazine sulphate. Selenium is said to be precipitated, tellurium not precipitated. Collect the precipitate on a Gooch crucible in the usual manner. The tellurium is precipitated from the filtrate by hydrogen sulphide. V. Lenher and C. H. Kao (*Journ. Amer. Chem. Soc.*, 47, 2454, 1925) recommend a similar process, using hydroxylamine hydrochloride as a reducing agent.

[2] Washing with warm water is inclined to transform the selenium into a soluble colloidal state (H. Schulze, *Journ. prakt. Chem.*, (2), 32, 390, 1886; A. Gutbier, *Zeit. anorg. Chem.*, 32, 51, 106, 1902).

[3] For converting selenium into the dioxide by burning it in a current of oxygen, see P. Klason and H. Mellquist, *Arkiv Kem. Min. Geol.*, 4, No. 18, 1, 1911.

[4] Some of the heavy metals may be partially precipitated by sulphur dioxide.

needs special attention. There is a maximum and a minimum concentration of the acid between which "best" results can be obtained. Keller's important experiments[1] on this subject show that, with hydrochloric acid of specific gravity 1·175 and with solutions containing 0·1000 grm. each of tellurium and selenium, the amounts of selenium and tellurium, which separated when solutions of different acidity were saturated in the cold with sulphur dioxide, were as follows :—

Table LIII.—*Effect of the Acidity of the Solution on the Precipitation of Selenium and Tellurium by Sulphur Dioxide.*

Acidity per cent.	Selenium.	Tellurium.	Acidity per cent.	Selenium.	Tellurium.
0·5	..	total	40	total	total
1	0	0·0761	50	total	total
2	..	0·0600	60	total	total
3	trace	0·0653	65	total	0·0965
5	0·0124	0·0745	70	total	0·0882
8	..	0·0931	75	total	0·0411
10	0·0349	total	80	total	nil
20	0·0800	total	90	total	nil
30	total	total	100	total	nil

These numbers are plotted in fig. 107. The left-to-right downwards cross-hatching shows where selenium is wholly precipitated; the right-to-left downwards cross-hatching shows where tellurium is wholly precipitated; and left-to-right and right-to-left cross-hatching shows where both tellurium and selenium are precipitated.

If selenium alone be present, total precipitation occurs if the acidity of the solution exceeds 30 per cent. If both selenium and tellurium be present, tellurium and selenium will all be precipitated if the acidity of the solution be kept between 30 and 60 per cent. But outside these limits either selenium or tellurium may be wholly or partially precipitated, according to the strength of the acid. Selenium will alone be precipitated from a mixed solution if the acidity of the solution exceeds 80 per cent.[2] Hence, if selenium be first precipitated from a solution over 80 per cent. acidity, and the solution made up to twice its former volume with water, the tellurium will be precipitated by a repetition of the sulphur dioxide treatment. The tellurium may be filtered off, dried and weighed in a similar manner to the process described for selenium.[3]

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[1] E. Keller, *Journ. Amer. Chem. Soc.*, 19, 771, 1897; C. Alexi, *Ueber die Bestimmung von Selen und Tellur und die Untersuchung von selen- und tellur-haltigen Handelskupfer*, Berlin, 1905.

[2] The precipitates are more voluminous from feebly acid solutions than from strongly acid solutions.

[3] For the reduction of tellurium solutions with hydrazine salts, see A. Rosenheim and M. Weinheber, *Zeit. anorg. Chem.*, 69, 266, 1910; P. Jannasch and M. Müller, *Ber.*, 31, 2377, 1898; A. Gutbier, *ib.*, 34, 2724, 1901; V. Lenher and A. W. Homberger, *Journ. Amer. Chem. Soc.*, 30, 387, 1908; V. Lenher and C. H. Kao, *ib.*, 47, 769, 1925; J. B. Menke, *Zeit. anorg. Chem.*, 77, 282, 1912; W. Geilmann and Fr. W. Wrigge, *Zeit. anorg. allgem. Chem.*, 210, 357, 1933. For the determination of tellurium in minerals, etc., see C. H. Fulton, *Journ. Amer. Chem. Soc.*, 20, 586, 1898; E. Keller, *ib.*, 19, 771, 1897; V. Lehner, *ib.*, 21, 347, 1899; V. Lenher and A. W. Homberger, *ib.*, 30, 387, 1908; E. Donath, *Zeit. angew. Chem.*, 3, 216, 1890; R. W. E. MacIvor, *Chem. News*, 86, 308, 1902; T. Egleston, *ib.*, 47, 51, 1883; C. Whitehead, *Journ. Amer. Chem. Soc.*, 17, 849, 1895; A. Gutbier and J. Huber, *Zeit. anal. Chem.*, 53, 430, 1914; F. A. Gooch and J. Howland, *Zeit. anorg. Chem.*, 7, 132, 1894;

Both volumetric[1] and colorimetric[2] processes have been proposed for the determination of selenium.

E. Kröner, *Chem. Ztg.*, **59**, 248, 1935; L. Moser and R. Miksch, *Monats.*, **44**, 349, 1914; O. E. Clauder, *Zeit. anal. Chem.*, **89**, 270, 1932. For the separation of antimony and tellurium, see W. Muthmann and E. Schröder, *Zeit. anorg. Chem.*, **14**, 437, 1897. For gold and tellurium, see V. Lenher, G. B. L. Smith and D. C. Knowles, junr., *Ind. Eng. Chem. Anal. Ed.*, **6**, 43, 1934.

[1] F. A. Gooch and A. W. Peirce, *Zeit. anorg. Chem.*, **11**, 249, 1896; *Amer. J. Sci.*, (4), **1**, 31, 1896; J. F. Norris and H. Fay, *Amer. Chem. Journ.*, **18**, 703, 1896; **23**, 119, 1901; W. Muthmann and J. Schäfer, *Ber.*, **26**, 1008, 1893; E. Divers and T. Shimidzu, *Journ. Chem. Soc.*, **47**, 441, 1885; P. Klason and H. Mellquist, *Arkiv Kem. Min. Geol.*, **4**, No. 18, 1, 1911; *ib.*, **4**, No. 29, 1, 1912; L. Losana, *Giorn. Chim. ind. appl.*, **4**, 464, 1922; L. A. Congdon and W. W. Bray, *Chem. News*, **128**, 266, 1924; L. Marino, *Zeit. anorg. Chem.*, **65**, 32, 1909; W. T. Schrenk and B. L. Browning, *Journ. Amer. Chem. Soc.*, **48**, 2550, 1926; Z. Littman, *Chem. Ztg.*, **51**, 323, 1927; O. Tomiček, *Bull. Soc. chim.*, **41**, (4), 1389, 1927; R. Berg and M. Teitelbaum, *Chem. Ztg.*, **52**, 142, 1928; E. Bennesch, *ib.*, **52**, 878, 1928; A. A. Borkovskiĭ and A. A. Babalova, *Zavodskaya Lab.*, **3**, 306, 1934; W. C. Coleman and C. R. McCrosky, *Ind. Eng. Chem. Anal. Ed.*, **9**, 431, 1937; *Journ. Amer. Chem. Soc.*, **59**, 1458, 1937.

[2] For the colorimetric determination of selenium, J. Jannek and J. Meyer (*Zeit. anorg. Chem.*, **83**, 51, 1913; *Ber.*, **46**, 2876, 1913) find that sodium hyposulphite gives a sensitiveness of 0·005 per cent. of SeO_2 in water or 0·002 per cent. in concentrated sulphuric acid; while with potassium iodide and starch, 5×10^{-7} grm. of selenium dioxide can be detected in 1 c.c. of solution, or five times that quantity in concentrated sulphuric acid. See also J. Meyer and W. von Garn, *Zeit. anal. Chem.*, **53**, 29, 145, 1914; S. Littmann, *Zeit. angew. Chem.*, **19**, 1039, 1081, 1906; A. Cousen, *Journ. Soc. Glass Tech.*, **7**, 303, 1923; W. O. Robinson, H. C. Dudley, K. T. Williams and H. G. Byers, *Ind. Eng. Chem. Anal. Ed.*, **6**, 274, 1934; **7**, 3, 1935; K. W. Franke, R. Burris and R. S. Hutton, *ib.*, **8**, 435, 1936; W. C. Hughes and H. N. Wilson, *Journ. Soc. Chem. Ind.*, **55**, 359T, 1936; S. T. Volkov, *Trans. All-Union Sci. Res. Inst. Econ. Mineral*, No. 98, 1936; *Zavodskaya Lab.*, **5**, 1429, 1936; V. K. Zemel, *ib.*, **5**, 1443, 1936. For the detection and determination of selenium in sulphuric acid by codeine phosphate, see E. Schmidt, *Arch. Pharm.*, **252**, 161, 1914; T. Raikhinstein (Z. Reichinstein), *Trans. Inst. Pure Chem. Reagents*, Moscow, **6**, 27, 1927; *Chem. Zentr.*, (1), 230, 1928. Compare R. C. Wells, *Journ. Wash. Acad. Sci.*, **18**, 127, 1928. For the determination of traces of selenium in sulphide minerals, see M. Schmidt, *Metall uud Erz*, **22**, 511, 1925; *Chem. Zentr.*, (1), 739, 1926; H. Lindhe, *Iva*, No. 2, 42, 1936. For a review of the analytical chemistry of selenium and tellurium, see M. Frommes, *Zeit. anal. Chem.*, **96**, 447, 1934.

CHAPTER XXXII.

THE DETERMINATION OF ALUMINIUM AND BERYLLIUM COMPOUNDS.

§ 238. The Gravimetric Determination of Alumina— Hess and Campbell's Process.

THE errors in the determination of the titanium and iron accumulate on the alumina. So also do the errors arising from an imperfect ignition of the mixed oxides ($Fe_2O_3 \rightarrow Fe_3O_4$), imperfect washings and imperfect separations. It is therefore interesting to find the magnitude of the error affecting the alumina under the conditions of the analysis by the process indicated in Part II. We have seen that with the clay in question there was an error of $\pm 0 \cdot 07$ per cent. in the determination of the titanic oxide, an error of $\pm 0 \cdot 06$ per cent. in the determination of the ferric oxide, and an error of $\pm 0 \cdot 13$ per cent. in the determination of the mixed oxides. Consequently the error in the determination of the alumina by difference[1] amounts to about $\pm 0 \cdot 09$ per cent. This is probably not far different from what would be obtained by a direct determination. The error does not multiply up as it did when the alkalies were determined by difference (page 214). The above estimate of the error becomes less favourable the less the proportion of alumina in the mixed precipitate and the greater the proportion of ferric oxide and titanic oxide. A small positive error in the determination of the two oxides—iron and titanium—might altogether mask small amounts of alumina. It is therefore desirable to use a direct method for the determination of small amounts of alumina in the presence of large amounts of iron.

Several processes have been suggested for the direct determination of alumina, but most of them are not very satisfactory in general work. The sodium thiosulphate process will be discussed later, when dealing with zirconium (pages 553, 562). Hess and Campbell[2] give a process which works well. After a critical examination of the method, Allen said that "minute quantities of alumina may be accurately separated from large amounts of iron by this process." It is based on the fact that aluminium hydroxide is quantitatively precipitated from solutions by the addition of phenylhydrazine. Any phosphorus which may be present will be precipitated with the aluminium

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[1] For the methods of calculation, see J. W. Mellor, *Higher Mathematics*, London, 518, 1926.

[2] W. H. Hess and E. D. Campbell, *Chem. News*, 81, 158, 1900; *Journ. Amer. Chem. Soc.*, 21, 776, 1899; E. T. Allen, *ib.*, 25, 421, 1903; *Chem. News*, 89, 43, 63, 76, 88, 103, 1904; M. Wunder and N. Chéladzé, *Ann. Chim. anal.*, 16, 205, 1911; F. L. Hahn and G. Leimbach, *Ber.*, 55B, 3161, 1922; S. Ishimaru, *Sci. Rep. Tôhoku Imp. Univ.*, (1), 25, 780, 1936; *Journ. Chem. Soc. Japan*, 53, 967, 1932; H. Honjo, *ib.*, 57, 682, 1936; H. H. Willard and N. K. Tang, *Ind. Eng. Chem. Anal. Ed.*, 9, 357, 1937.

hydroxide as aluminium phosphate. Chromium,[1] titanium, zirconium [2] and thorium,[3] if present, will be precipitated with the aluminium hydroxide; but ferrous iron,[4] beryllium,[5] manganese, zinc, cobalt, nickel, cadmium, mercury, magnesium, barium, strontium and calcium will not be precipitated.[6]

First Precipitation.—The solution is diluted to 100 or 200 c.c., according to the amount of alumina to be precipitated, and heated to about 90°. Ammonia is added until the precipitate formed just redissolves. Add 5 to 20 drops, according to the amount of iron in solution, of a neutral saturated solution of ammonium bisulphite,[7] with constant stirring, until the solution smells strongly of sulphur dioxide. If the solution turns deep red, it is not acid enough. The red colour shows that ferric sulphite is present. In that case, add a few drops of hydrochloric acid, then add ammonia quickly [8] to make the solution neutral as before. Add a couple of drops of dilute hydrochloric acid. Add phenylhydrazine [9] (1 to 3 c.c.), with constant stirring, to the liquid smelling strongly of sulphur dioxide, until all the alumina is precipitated. When the precipitate has become flaky and settles quickly, filter as usual. The filtration should be done quickly or a brownish scum may form on the surface of the solution and on the sides of the beaker. The solution should not stand more than an hour before filtration. The precipitate is generally coloured brown. The colouring agent is not necessarily ferric hydroxide, but rather organic impurities in the precipitating agent. Wash the precipitate with hot water containing dilute phenylhydrazine bisulphite [10] in solution. Continue the washing until the wash-water gives no indication of iron when

[1] The precipitation of chromium is slowest in chloride solutions and quickest in nitrate and sulphate solutions.

[2] A. M. Jefferson (*Journ. Amer. Chem. Soc.*, 24, 543, 1902) says that zirconium is not precipitated by phenylhydrazine, but Allen shows that this is a mistake. Titanium and zirconium can be separated from beryllium in chloride solutions by this precipitant.

[3] Thorium is precipitated completely from nitrate solutions, cerium only partially.

[4] Phenylhydrazine is a powerful reducing agent, and it thus plays a double rôle: (1) maintaining the iron in the ferrous condition; and (2) precipitating the alumina. Ferric oxide, it may be added, is partially precipitated by phenylhydrazine. It is necessary to convert the ferric into ferrous salts before adding the phenylhydrazine, because the latter does not reduce ferric salts very rapidly.

[5] Beryllium is not precipitated from chloride solutions, but a large proportion is precipitated from sulphate solutions and a trace from nitrate solutions. The method for the separation of aluminium and chromium from beryllium by this process, which naturally here suggests itself, does not work.

[6] If zinc, cobalt, nickel, mercury or cadmium be present in concentrated solution the corresponding hydroxides may be precipitated. Molybdenum salts give a bright red coloration—L. Spiegel and T. A. Maass, *Ber.*, 36, 512, 1903.

[7] AMMONIUM BISULPHITE SOLUTION.—Pass sulphur dioxide from a syphon of the liquefied gas into a cooled solution of ammonia (1 : 1) until the solution becomes yellow. The object of the sulphur dioxide is not only to reduce the iron, but to keep it in the reduced condition so as to prevent its precipitation with the alumina.

[8] If the operation be done slowly, some ferric hydroxide may be formed which does not dissolve readily in the dilute hydrochloric acid.

[9] To prevent a waste, it is best to add 1 or 2 c.c. of phenylhydrazine and, if no precipitate is formed, add dilute ammonia drop by drop until a precipitate is just visible. Clear this up by adding one drop of acid and add more phenylhydrazine. If too little phenylhydrazine has been added, a few drops of the filtrate will show the mistake. The phenylhydrazine should be free from foreign organic matter. Tin has been detected in commercial samples. For its preservation, see G. Denigés, *Bull. Trav. Soc. Pharm. Bordeaux*, 52, 513, 1912; F. D. Chattaway, *Chem. News*, 103, 217, 1911.

[10] PHENYLHYDRAZINE BISULPHITE SOLUTION.—Add a cold saturated solution of sulphurous acid gradually to a few cubic centimetres of phenylhydrazine until the precipitate of phenylhydrazine sulphite, first formed, redissolves to a yellow solution. If the odour of sulphur dioxide appears after standing a few minutes, add a few drops of phenylhydrazine to neutralise the sulphur dioxide. This solution keeps indefinitely in a well-stoppered bottle. For use, mix from 5 to 10 c.c. of the solution so prepared with 100 c.c. of hot water.

mixed with a few drops of ammonium sulphide, and no indication of chlorides. Test the filtrate with a couple of drops of phenylhydrazine to make sure that precipitation is complete.

Second Precipitation.—It is best to redissolve the precipitate on the filter-paper in hot dilute hydrochloric acid; wash the paper well with hot water; neutralise the solution with ammonia; acidulate with a couple of drops of hydrochloric acid (1 : 1); and precipitate the aluminium hydroxide from the small volume of liquid by the addition of, say, 0·5 c.c. of phenylhydrazine. Wash as before.

The Ignition.—The filter-paper is dried in a platinum crucible, charred at a low temperature and ignited at a bright red heat until its weight is constant. A second ignition is always advisable to make sure the weight is really constant. Weigh as alumina—Al_2O_3.

Errors.—Allen found that when aluminium hydroxide is precipitated from pure solutions the results are inclined to be rather low. For example: Used, 0·2500 grm. Al_2O_3; found, 0·2487 grm. Al_2O_3; error, −0·0013 grm. But the separation of aluminium, titanium and zirconium from iron, in a solution containing a mixture of all four salts, gave excellent results. Thus:

Used	.	.	0·1817	0·1648	0·1059	0·0726	0·0595 grm.
Found	.	.	0·1816	0·1654	0·1063	0·0717	0·0603 grm.
Error	.	.	−0·0001	+0·0006	+0·0004	−0·0009	+0·0008 grm.

If phosphorus be present, it must either be determined on a separate sample, or the ignited alumina fused with sodium carbonate or potassium bisulphate (page 166), and the phosphorus determined as indicated on page 672. If the phosphorus be in excess of that required to form aluminium phosphate —$AlPO_4$—Hess and Campbell recommend the addition of an excess of a solution of aluminium chloride of known strength, and proceeding as indicated above, making due allowance for the extra alumina.

If desired, the alumina and iron may be precipitated with ammonia in the usual way (page 164), or by the basic acetate process (page 383), and the alumina precipitated as indicated above from the pyrosulphate fusion. The iron can be determined by difference, or precipitated with ammonium sulphide.[1] Other methods for the separation of aluminium and iron have been proposed.[2]

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[1] Along with other metals precipitated by that reagent, if such elements be present.

[2] For an examination of the various methods for aluminium, see N. Levine, *Bull. Inst. Meurice*, 2, 24, 1912; *Circular, Bureau Standards*, No. 26, 1913. For the separation by cupferron, see J. Brown, *Journ. Amer. Chem. Soc.*, 39, 2358, 1917; by o-phenetidine, K. Chalupny and K. Breisch, *Zeit. angew. Chem.*, 35, 233, 1922; by hydrazine carbonate, J. Lukas and A. Jilek, *Coll. Czech. Chem. Comm.*, 24, 2962, 1930; T. Kozu, *Journ. Chem. Soc. Japan*, 54, 682, 1933; by 8-hydroxyquinoline, R. Berg, *Zeit. anal. Chem.*, 76, 191, 1929; T. Heczko, *Chem. Ztg.*, 58, 1032, 1934; W. Steger, *Ber. Deut. ceram. Ges.*, 16, 624, 1935; S. Yu Fainberg and E. M. Tel, *Zavodskaya Lab.*, 5, 1307, 1936. For other methods, see G. van Pelt, *Bull. Soc. chim. Belg.*, 28, 101, 138, 1914; P. Wenger and J. Wuhrmann, *Ann. Chim. anal.*, (2), 1, 337, 1919; H. Borck, *Chem. Ztg.*, 38, 7, 1914; H. D. Minnig, *Amer. J. Sci.*, (4), 39, 197, 1915; S. Palkin, *Journ. Ind. Eng. Chem.*, 9, 951, 1917; E. S. v. Bergkampf, *Zeit. anal. Chem.*, 83, 345, 1931; W. R. Ormandy, *Journ. Inst. Chem.*, 126, 1933; E. C. Pigott, *Ind. Chemist*, 12, 360, 1936; P. N. Grigor'ev and V. G. Dubovitskaya, *Ogneupory*, 5, 105, 1937. For colorimetric processes, see F. W. Atack, *Journ. Soc. Chem. Ind.*, 34, 936, 1915; I. M. Kolthoff, *Chem. Weekb.*, 24, 447, 1927; P. S. Roller, *Journ. Amer. Chem. Soc.*, 55, 2437, 1933; J. H. Yoe and W. L. Hill, *ib.*, 49, 2395, 1927; V. C. Myers, J. W. Mull and D. B. Morrison, *Journ. Biol. Chem.*, 78, 595, 1928; E. W. Schwartze and R. M. Hann, *Science*, 69, 167, 1929; A. P. Mussakin, *Zeit. anal. Chem.*, 105, 351, 1936; A. K. Babko, *Univ. état Kiev Bull. sci. Recueil chim.*, 2, No. 2, 59, 1936. For the volumetric determination of aluminium, see A. Stock, *Compt. rend.*, 130, 175, 1900; *Ber.*, 33, 548, 1900; S. E. Moody, *Zeit. anorg. Chem.*, 46, 424, 1905; *Amer. J. Sci.*, (4), 20, 181, 1905; I. P. Osipov, *Journ. Russ. Phys. Chem. Soc.*, 47, 613, 1915; T. v. Kovscharova, *ib.*, 47, 616, 1915; V. N. Ivanov, *ib.*, 46, 419, 1914.

§ 239. The Analysis of Bauxite.

An accurate and complete analysis of this mineral can be made by a process similar to that used for clays.[1] Time may be saved in analyses for commercial work by using, say, Handy's process,[2] which may be regarded as a type of many others. Here the mineral is decomposed by aqua regia so as to avoid an undesirable accumulation of alkali salts in the filtrate.[3] Mix 1·5 grms. of the finely powdered bauxite, dried at 100°, with 50 c.c. of acid,[4] in a 300–350 c.c. evaporating basin. Evaporate the solution until white fumes are evolved and continue heating the mixture for another 15 minutes. Cool. Add 100 c.c. of water; stir; boil for 10 minutes. The silica is thus dehydrated and precipitated. Filter the solution into a 300 c.c. beaker. Wash the precipitate with water. The filtrate and washings will occupy between 150 and 200 c.c.

The insoluble matter [5] is ignited in a platinum crucible and weighed. Add 3–4 drops of sulphuric acid and about 5 c.c. of hydrofluoric acid. Evaporate slowly to dryness. Ignite and weigh. The loss in weight represents silica. Fuse the residue with a little potassium bisulphate. When all is dissolved, cool. Take up the mass with water and add the solution to the main solution. Any insoluble residue will be silica, which is filtered off, ignited and weighed. The weight is added to the previous result for silica. Make the mixed solution up to 300 c.c.

Divide the 300 c.c. into three portions of 100 c.c. In one, precipitate a mixture of alumina, titanic oxide and ferric oxide with ammonium chloride and ammonia.[6] The filtrate from this solution is used for the determination of lime (page 202) and magnesia (page 208).[7] The precipitate is washed, ignited and weighed (page 165). The titanium can be determined, if necessary, by the gravimetric process (page 193).[8] In the second 100 c.c., determine the iron by reduction with zinc and the permanganate titration (page 169).[9] The

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[1] For an exhaustive account of the analysis of bauxite and high-alumina refractories, see G. E. F. Lundell and J. I. Hoffman, *Bur. Stand. Journ. Research*, **1**, 91, 1928. Compare W. Singleton, *Chem. Age—China Clay Rev. Sect.*, **6**, July 16th; **6**, Aug. 20th, 1927; E. P. Barrett and F. W. Schroeder, *Journ. Amer. Cer. Soc.*, **8**, 69, 1925.

[2] J. O. Handy, *Journ. Amer. Chem. Soc.*, **18**, 766, 1896; H. Lienau, *Chem. Ztg.*, **27**, 422, 1903; **29**, 1280, 1905; M. Taurel, *Ann. Chim. anal.*, **9**, 323, 1904. For a rough method of evaluating aluminous minerals, see J. C. y León, *Anales Soc. Espan. Fis. Quim.*, **8**, 281, 1911. For the determination of free alumina in bauxite, see E. Martin, *Chim. et Ind.*, Special No. 200, 1926.

[3] For fusion with sodium peroxide, see W. Trautmann, *Zeit. angew. Chem.*, **26**, 702, 1913. J. E. Gieseking and H. J. Snider (*Ind. Eng. Chem. Anal. Ed.*, **9**, 233, 1937) recommend a mixture of sodium carbonate, 2 parts, and lithium carbonate, 1 part, m. pt. 470°–480°, for fusing highly aluminous minerals at a temperature of 500°–600°.

[4] Acid mixture: 100 c.c. of nitric acid (sp. gr. 1·42), 300 c.c. of hydrochloric acid (sp. gr. 1·20), and 600 c.c. of sulphuric acid (sp. gr. 1·18). E. Martin (*Ann. Chim. anal.*, **18**, 297, 1913; *Monit. Scient.*, (5), **3**, 232, 1913) heats one gram of the mineral in a flask with 15 c.c. of aqua regia (equal volumes) and 30 c.c. of dilute sulphuric acid (1 : 1 by volume) until dense white fumes appear and solid sulphates begin to separate. The residue is dissolved in 50 c.c. of water, the silica filtered off and purified in the usual way.

[5] According to E. Baud (*Rev. Chim. pure appl.*, **6**, 368, 1903), the residue will contain in addition to silica, titanic oxide, corundum, if present, and a little alumina. These are subsequently brought into solution by the potassium bisulphate fusion, as described in the text.

[6] This method will give low results if a great excess of ammonium chloride is not used (page 162).

[7] K. W. Jurich, *Die Fabrikation von schwefelsaurer Tonerde*, Berlin, 45, 1894.

[8] See H. J. Winch and V. L. Chandratreya, *Chem. News*, **124**, 231, 1922, for the volumetric determination of titanium in bauxite.

[9] There is the difficulty with permanganate titrations mentioned on page 171, when much titanium is present. In that case special precautions must be adopted (see page 172).

alkalies are determined by Smith's process[1] (page 214); the loss on ignition (organic matter and water), as on page 136.[2]

§ 240. The Analysis of Alumina—Hydrated and Calcined.

The alumina "hydrate" on the market may have from about 40 to 65 per cent. of Al_2O_3. It is sometimes sold with a guarantee of 60 per cent. Al_2O_3. The loss on ignition (page 136) includes water and carbon dioxide. For the silica, heat 5 grms. of the hydrate with 25 c.c. of sulphuric acid (sp. gr. 1·4). The alumina dissolves. Cool. Add 100 c.c. of water and boil. The insoluble silica separates. Filter, wash and ignite the insoluble matter in a platinum crucible and weigh. Treat the residue with sulphuric and hydrofluoric acids as described above. Weigh again. The loss in weight represents silica. Fuse the residue with potassium bisulphate, take up with water, and add to the main solution. The iron can be determined colorimetrically in this solution (page 185).

The sodium can be determined (1) by difference, using Smith's process (page 214), with separation of the potassium as perchlorate from the mixed chlorides (page 224); or (2) directly, by separation from the mixed chlorides as triple acetate (page 236); or, better still, (3) the sodium can be determined by calcining 5 grms. of the "hydrate" at a red heat,[3] and digesting the calcined mass on a water bath with an excess of $1·0N$-H_2SO_4, and titrating back with $1·0N$-NaOH (page 58). This gives the "total sodium." The "soluble sodium" is determined by boiling 5 grms. of the "hydrate" in water and titrating the filtered solution with $1·0N$-H_2SO_4, using phenolphthalein as indicator. The difference between the "total" and the "soluble" sodium represents the "combined" sodium. Calculate the percentage of CO_2 corresponding to the percentage of "soluble" sodium found, and subtract the result from the percentage loss on ignition. The difference represents water. The alumina is usually determined by difference, although it can be determined by precipitation from an aliquot portion of the main solution as indicated under bauxite.

Calcined alumina[4] may contain 99 per cent. of alumina. Fuse a gram of the dried alumina with, say, 10 grms. of potassium bisulphate. If the molten mass be not clear, add 2 more grams of the flux to the cold mass and fuse again. Dissolve the cold mass in water. Filter off the insoluble residue and fuse it with sodium carbonate. Take up the cold mass with water in a 300 c.c. evaporating basin. Add 25 c.c. of dilute sulphuric acid and, when the action has subsided, evaporate the solution until the sulphuric acid begins to fume. Cool; add 100 c.c. of water. Boil the solution. Filter, wash, ignite and weigh the residue. Treat the residue with sulphuric acid and hydrofluoric acid as

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[1] See E. B. Read, *Journ. Amer. Ceram. Soc.*, 18, 341, 1935.

[2] Bauxites may contain many minor constituents, *e.g.* small quantities of the oxides of nickel, manganese, chromium, vanadium, phosphorus, and traces of beryllium are present in Hungarian bauxites—*Ind. Eng. Chem. News Ed.*, 11, 110, 1933.

[3] This is to make the alumina insoluble in acid. Note: too strong ignition may result in the loss of alkali.

[4] Alundum is made by fusing bauxite in the electric furnace. It contains about 1 per cent. of silica, ferric and titanic oxides. Alundum is scarcely attacked by aqueous acids and alkalies, and it is but superficially attacked by fused alkali carbonates. For the opening up of aluminous material and silicates, see R. W. Ellison, *Journ. Amer. Ceram. Soc.*, 10, 463, 1927. A. N. Finn and J. F. Klekotka (*Bur. Stand. Journ. Research*, 4, 809, 1930) heat 0·5 grm. of the powdered substance with 0·6 grm. of sodium carbonate for 2 hours at 875°. The resulting sintered mass is easily decomposed by hydrochloric acid.

described under bauxite. Ignite and weigh again. The loss represents silica. For sodium, use Smith's process. The alumina is generally determined by difference. These methods will suffice to show adulterations with china clay or ground flint.[1]

§ 241. The Analysis of Cryolite.

Silica.—Although cryolite contains a large amount of fluorine, the relatively small amount of silica, which is also present, does not all react with the fluorine, to form volatile silicon fluoride, when the powdered mineral is digested with sulphuric acid. Part remains with the residue undecomposed. This fact makes the determination a little laborious. The silica must be sought both in the residue and in the escaping gases. The solutions cannot be acidified with hydrochloric acid and evaporated in the usual manner, because some silica would be then lost as silicon fluoride. Fresenius and Hintz [2] recommend a process which certainly has not the merit of simplicity. The method indicated on page 725 may be here used. Fuse the cryolite with an excess of sodium carbonate and extract the melt with water.[3] Precipitate silica, alumina, lime, etc., with Seemann's solution, and determine the silica, etc., as indicated on page 731.[4] For the sodium, use Smith's process (page 214). The processes indicated on pages 731 to 741 are available for fluorine.

§ 242. The Detection of Beryllium.

If beryllia be present, it will invariably be found associated with the alumina and ferric oxide precipitated by ammonia. The properties of beryllia are closely related to those of alumina. In testing for beryllium,[5] the silica is separated by evaporation, and the hydrogen sulphide group precipitated in acid solution in the usual manner. The filtrate is evaporated down to about 25 c.c., and, when *cold*, add a couple of grams of sodium peroxide (solid). Boil and filter the alkaline solution; acidify the filtrate with nitric acid and add an excess of ammonia. If no precipitate be formed, beryllium is absent; if a precipitate be formed, transfer it to a small beaker containing 2 or 3 grms. of solid sodium bicarbonate per 20 c.c. of liquid (10 per cent. solution). Raise the temperature rapidly to boiling, and boil half a minute. Alumina is precipitated. Filter. Dilute the filtrate with 10 volumes of water (so as to make approximately a 1 per cent. solution) and boil. If beryllium be present, a precipitate will be formed.

To distinguish beryllia from alumina, dissolve the precipitate in acid [6];

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[1] For a discussion of procedures and conditions to be adopted in the analysis of silico-aluminous compounds for industrial control, see E. Delfeld, *Bull. Soc. chim. Belg.*, 40, 427, 1931; 41, 202, 1932. J. Delforge (*ib.*, 41, 95, 1932) criticises these methods.

[2] C. R. Fresenius and E. Hintz, *Zeit. anal. Chem.*, 28, 324, 1889. See also F. J. Frere, *Ind. Eng. Chem. Anal. Ed.*, 6, 124, 1934; A. A. Borkovskiĭ and N. A. Porfin'ev, *Journ. Applied Chem. (U.S.S.R.)*, 7, 623, 1934.

[3] E. C. Uhlig (*Chemical Analysis for Glassmakers*, Pittsburg, 80, 1903) recommends fusing the cryolite with sodium carbonate as it if were a typical silicate. He ignores the action of the fluorides on the porcelain basin, on the precipitation of alumina (page 160), and the volatilisation of silica as silicon fluoride.

[4] The filtrate is used for the fluorine determination (page 725).

[5] C. L. Parsons, *The Chemistry and Literature of Beryllium*, Easton, Pa., 6, 1908.

[6] Freshly precipitated beryllium hydroxide is readily soluble in potassium or ammonium carbonate, sodium hydroxide, or dilute acids. If the hydroxide be allowed to stand for some time at ordinary temperatures, or if it be heated with water, dilute ammonia, alkali carbonates or alkali hydroxides, it appears to become very sparingly soluble in these menstrua—
—F. Haber and G. van Oordt, *Zeit. anorg. Chem.*, 38, 377, 1904.

nearly neutralise the solution with ammonia; add ammonium carbonate. The white precipitate may be either aluminium or beryllium hydroxide. The latter alone is soluble in an excess of the reagent, and a white precipitate of basic carbonate is obtained on boiling the clear solution.[1] Again, both aluminium and beryllium salts give white precipitates with caustic soda; with both, the precipitates are soluble in an excess of the reagent; but only beryllia is precipitated on boiling.

Fischer's Test.[2]—A few drops of a 5 per cent. solution of quinalizarin (1 : 2 : 5 : 8-tetrahydroxyanthraquinone) in 0·25N-sodium hydroxide are added to 10 c.c. of the solution under test, which is then made alkaline with 0·25N-sodium hydroxide. If beryllium is present, a blue colloidal solution is obtained. It is advisable to compare the colour with the violet colour given by a blank test with 0·25N-sodium hydroxide solution. Sufficient sodium hydroxide must be present to keep the aluminium in solution and, if iron is also present, tartaric acid must be added. Magnesium gives a similar blue colour, but, if an ammoniacal solution of the reagent be added to the neutral solution under test, the subsequent addition of bromine water flocculates the beryllium complex, whereas the magnesium complex is entirely destroyed. The test is said to detect $1·5 \times 10^{-6}$ grm. of beryllium per c.c. in solutions containing 2 mgrms. of magnesium or 6 mgrms. of aluminium per c.c.

Beryllium, by the way, is sometimes called "glucinum" and symbolised Gl.

§ 243. The Gravimetric Determination of Beryllium— Parsons and Barnes' Process.

Beryllia is precipitated with alumina by ammonia, sodium thiosulphate and sodium acetate or ammonium formate.[3] When beryllium is present, four points require special attention in the treatment of the ammonia precipitate:— (1) Ammonia does not give complete precipitation unless ammonium chloride be present. (2) When the precipitate is washed with water and the ammonium chloride has nearly all gone, the beryllium hydroxide begins to pass through the paper, and this more rapidly than is the case with alumina under similar conditions. The addition of ammonium salts—say ammonium acetate—to the water used for washing effectively prevents this action and the washing then presents no difficulty of this nature. (3) If the solution be boiled to drive off the ammonia, beryllium hydroxide will redissolve, so that cold precipitations give the best results. (4) Small amounts of beryllium hydroxide may adhere very tenaciously to the walls of the vessel in which the precipitation is made.[4] Hence, after as much beryllia has been removed as is convenient, it is advisable to wash the walls with a little dilute nitric acid, and re-precipitate the beryllia which has been dissolved.

The beryllia found in the ammonia precipitate along with, say, iron,

[1] M. Wunder and N. Chéladzé, *Ann. Chim. anal.*, **16**, 205, 1911. Beryllia dissolves but slowly in the ammonium carbonate, according to G. N. Wyrouboff (*Bull. Soc. chim.*, (3), **27**, 733, 1902; *Chem. News*, **86**, 67, 1902), and a little alumina may also dissolve, if it is not precipitated by heat or by long contact with the solution.

[2] H. Fischer, *Wiss. Veröff. Siemens-Konz.*, **5**, 99, 1926; *Zeit. anal. Chem.*, **73**, 54, 1928. For the detection of beryllium by *p*-nitrobenzeneazo-orcinol, see A. S. Komarovskii and N. S. Poluektov, *Mikrochem.*, **14**, 315, 1934. For a review of methods for the detection of beryllium, see M. Frommes, *Zeit. anal. Chem.*, **93**, 285, 1933.

[3] C. A. Joy, *Amer. Journ. Sci.*, (2), **36**, 83, 1863; *Chem. News*, **8**, 183, 197, 1863.

[4] B. Bleyer and K. Boshart (*Zeit. anal. Chem.*, **51**, 748, 1912) studied the precipitation of beryllium by ammonia and by ammonium sulphide in ordinary glass, in Jena glass, in porcelain and in platinum vessels. The two last-named gave the best results.

chromium and aluminium oxides can be separated by fusing the precipitate for two or three hours with sodium carbonate; the beryllia remains with the iron [1] on washing with water, while the aluminium and chromium pass into solution as aluminate and chromate. The beryllia and iron can be separated by fusion with sodium pyrosulphate, leaching with water and precipitating the iron with potassium hydroxide. The precipitate is filtered and washed; the filtrate is acidified with hydrochloric acid and the beryllia precipitated by ammonia.[2]

Parsons and Barnes' [3] process for the quantitative separation of beryllium is based on the insolubility of aluminium and ferric hydroxides in a 10 per cent. solution of sodium bicarbonate and the ready solubility of beryllium hydroxide [4] in the same reagent.

First Precipitation of Aluminium and Iron.—After the first precipitation by ammonia,[5] the hydroxides are dissolved in hydrochloric acid and oxidised, if necessary, with a drop of hydrogen peroxide or nitric acid.[6] Neutralise the solution with ammonia, and to the *cold* solution add 10 grms. of solid sodium bicarbonate [7] per 100 c.c. of solution. Cover the beaker [8] with a clock-glass, and heat the solution to boiling as quickly as possible.[9] Boil the solution one minute.[10] Place the beaker in cold water and, when cold, filter. Collect the filtrate in a litre beaker and wash the residue three times with a hot (70°–80°) 10 per cent. solution of sodium bicarbonate.

Second Precipitation of Aluminium and Iron.—The precipitated ferric and aluminium hydroxides generally retain a little beryllium.[11] Hence the precipitate is re-dissolved off the filter-paper in as little dilute hydrochloric acid

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[1] B. E. Dixon (*Analyst*, 54, 268, 1929) separates titanium from beryllium by precipitating the former as hydroxide with *p*-chloroaniline.

[2] M. Wunder and P. Wenger, *Zeit. anal. Chem.*, 51, 470, 1912; W. R. Schoeller and H. W. Webb, *Analyst*, 61, 235, 1936; B. E. Dixon, *ib.*, 54, 268, 1929. Usually two fusions are necessary—H. T. S. Britton, *Analyst*, 47, 50, 1922.

[3] C. L. Parsons and S. K. Barnes, *Journ. Amer. Chem. Soc.*, 28, 1589, 1906; S. L. Penfield and D. N. Harper, *Amer. J. Science*, (3), 32, 112, 1886; *Chem. News*, 54, 90, 102, 1886; F. A. Gooch and F. S. Havens, *Zeit. anorg. Chem.*, 13, 435, 1896; F. S. Havens, *ib.*, 16, 15, 1898; L. A. Aars, *Ueber die analytische Bestimmung von Beryllium und den sogenannten selten Erden*, Kristiania, 1905; H. T. S. Britton, *Analyst*, 46, 359, 437, 1921; C. L. Parsons, *The Chemistry and Literature of Beryllium*, Easton, Pa., 1909. H. Fischer and G. Leopoldi (*Wiss. Veröff. Siemens-Konz.*, 10, 1, 1931) condemn the method.

[4] Uranium, if present, also dissolves. For the separation of uranium from beryllium by precipitation as ferrocyanide, see W. R. Schoeller and H. W. Webb, *Analyst*, 61, 235, 1936. Compare M. Wunder and P. Wenger, *Zeit. anal. Chem.*, 53, 371, 1914.

[5] In the case of the basic acetate separation, C. L. Parsons (*Journ. Amer. Chem. Soc.*, 26, 738, 1904; C. L. Parsons and W. O. Robinson, *ib.*, 28, 555, 1906) proposes to separate beryllium from iron and aluminium by digesting the mixed precipitate in hot glacial acetic acid, which dissolves basic beryllium acetate from the dried precipitate and, after filtering the solution through a hot-water funnel, basic beryllium acetate separates from the solution on cooling. The small amounts of ferric and aluminium acetates which dissolve do not separate on cooling. F. Haber and G. van Oordt (*Zeit. anorg. Chem.*, 40, 465, 1904) propose to separate beryllium from the mixed basic acetates by treatment with chloroform, in which the basic beryllium acetate dissolves. For the separation of iron from beryllium by cupferron, see A. Tettamanzi, *Industria Chimica*, 9, 752, 1934.

[6] Although hydrogen peroxide is usually a better oxidising agent than nitric acid, it is far more likely to introduce impurities into the solution than is pure nitric acid. "Analytical reagent" hydrogen peroxide should be used—J. V. Dubsky and E. Krametz, *Mikrochem.*, 20, 57, 1936.

[7] Free from all but traces of sodium carbonate as shown by the phenolphthalein test—page 50.

[8] When the solution is warmed, loss by spitting may occur, if the beaker be not covered.

[9] If too much carbon dioxide be lost on boiling, aluminium may pass into solution.

[10] The brisk evolution of carbon dioxide must not be mistaken for boiling.

[11] And uranium, if present.

(1 : 1) as possible. Collect the solution in the beaker in which the precipitation was first made. Make the solution up to about 100 c.c., neutralise with ammonia and treat the mixture as the first one was treated.[1] Collect the filtrate and washings in the same litre beaker. To the combined filtrates 5–10 c.c. of colourless ammonium sulphide are added to precipitate the last traces of iron. The solution is well stirred and allowed to stand in the cold until the iron precipitate coagulates and settles. It is then filtered and the precipitate washed.

Third Precipitation of Aluminium and Iron.—It is impracticable to wash the sodium bicarbonate from the precipitated ferric and aluminium hydroxides; hence it is best to dissolve the precipitate in dilute hydrochloric acid and re-precipitate the iron and aluminium hydroxides with ammonia in the ordinary way (page 164).

Precipitation of Beryllium.—The final filtrate from the aluminium and iron precipitations is carefully acidified with concentrated hydrochloric acid with the beaker covered so as to avoid "spurting losses" by the escaping gas.[2] Boil the solution to remove carbon dioxide.[3] Add a slight excess of ammonia, boil, let the precipitate settle, filter and wash with ammonium acetate (2 per cent. solution) until the washings are free from chlorides. Ignite and weigh as beryllium oxide—BeO.

The Accuracy of the Separation.—In illustration of the accuracy of the method of separation, Parsons and Barnes quote the following separations with mixtures of varying proportions of ferric, aluminium and beryllium chlorides when the two former were several times the amount of the latter:

| Used | . | . | 0·2152 | 0·0911 | 0·0825 | 0·1020 | grm. BeO. |
| Found | . | . | 0·2146 | 0·0906 | 0·0806 | 0·0995 | grm. BeO. |

Hence the "separation is almost complete. The resulting beryllia was found to be analytically pure." Consequently, the method of separation just described "leaves little to be desired." [4]

§ 244. Kolthoff and Sandell's Process.

Kolthoff and Sandell have shown that 8-hydroxyquinoline precipitates aluminium and iron but not beryllium from slightly acid solutions, and subsequent work has indicated that this is probably the best method to date for the separation of beryllium from aluminium and iron.[5]

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[1] A cloudiness in the filtrate is probably due to the dilution of the concentrated solution of sodium bicarbonate with water.

[2] Just before neutralisation, some beryllium may be precipitated but this redissolves on adding more acid.

[3] Otherwise ammonium carbonate may be formed later on. Beryllium hydroxide is soluble in ammonium carbonate solutions.

[4] H. T. S. Britton (*Analyst*, 46, 359, 437, 1921) says the separation is satisfactory if the amount of aluminium or beryllium in 100 c.c. of saturated sodium bicarbonate solution does not respectively exceed 0·15 grm. and if adsorption is minimised by vigorous stirring during each precipitation.

[5] I. M. Kolthoff and E. B. Sandell, *Journ. Amer. Chem. Soc.*, 50, 1900, 1928; M. Niesser, *Zeit. anal. Chem.*, 76, 135, 1929; L. Fresenius and M. Frommes, *ib.*, 87, 273, 1932; 93, 275, 1933; G. E. F. Lundell and H. B. Knowles, *Bur. Stand. Journ. Research*, 3, 91, 1929; H. Thurnwald and A. A. Benedetti-Pichler, *Mikrochem. Emich Festschr.*, 1, 1930; *Mikrochem.*, 9, 324, 1931; 11, 200, 1932; H. V. Churchill, R. W. Bridges and M. F. Lee, *Ind. Eng. Chem. Anal. Ed.*, 2, 405, 1930; F. G. Hills, *ib.*, 4, 31, 1932; H. Fischer and G. Leopoldi, *Wiss. Veröff. Siemens-Konz.*, 10, 1, 1931; V. M. Zvenigorodskaya and T. N. Smirnova, *Zeit. anal. Chem.*, 97, 323, 1934; L. F. Kerley, *Journ. Proc. Australian Chem. Inst.*, 4, 223, 1937; O. Hackl, *Zeit. anal. Chem.*, 109, 91, 1937.

The slightly acid solution, which should not contain more than 0·1 grm. of aluminium or beryllium oxide per 100 c.c., is warmed to 50°–60° and then treated with excess of an acetic acid solution of the reagent.[1] In ordinary cases, where alumina preponderates, a 10–20 per cent. excess of the reagent is sufficient, but when there is much beryllia and little alumina present, at least a 50 per cent. excess should be used. A 2N-solution of ammonium acetate is then slowly added until a permanent precipitate is obtained, and then 20–25 c.c. more of the ammonium acetate solution, to ensure complete precipitation of aluminium and iron. The solution is filtered and the precipitate well washed with cold water.[2] The filtrate is heated to boiling and ammonium hydroxide added drop by drop until the liquid smells faintly of ammonia. The precipitated beryllium hydroxide is coloured yellow to brown by the adsorbed precipitant. After filtering, the precipitate is washed with a hot dilute solution of ammonium acetate, made just alkaline with ammonia. After drying and charring the paper, the precipitate is ignited to constant weight, cooled and *rapidly* weighed. With small quantities of beryllia, it is advisable to convert to the anhydrous sulphate and weigh as such.[3] Hence the oxide is moistened with a few drops of sulphuric acid (1 : 1), the mixture evaporated to dryness and the residue ignited at 350°–450°. The results by this method tend to be slightly high.[4]

Hills points out that, when relatively large quantities of aluminium and iron oxides [5] are present, the hydroxyquinoline precipitate is very bulky and awkward to manipulate and, moreover, that a re-solution and re-precipitation are essential. Thus, he finds it more satisfactory to combine the hydroxy-quinoline with the Parsons-Barnes process as follows: After making the bicarbonate precipitations, the filtrate is acidified and to the slightly acid solution is added an excess of a 2·5 per cent. solution of 8-hydroxyquinoline in acetic acid, followed by 20–25 c.c. of saturated ammonium acetate solution. The precipitate is filtered off and washed and the beryllia precipitated in the filtrate with ammonia. As wash liquor for the beryllia, Hills uses a 2 per cent. solution of ammonium nitrate.

A number of other methods have been published for the separation of beryllium.[6]

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[1] HYDROXYQUINOLINE REAGENT.—Dissolve 5 grms. of the finely powdered substance in 100 c.c. of 2N-acetic acid.

[2] If filtered through a Gooch crucible, or preferably a Jena glass or porcelain filter crucible, the precipitate can be dried at 120°–140° and weighed as $(C_9H_6ON)_3Al$ with 11·10 per cent. Al_2O_3, if iron is absent. Lundell and Knowles (*l.c.*) recommend decomposition of the organic matter with nitric and sulphuric acids, followed by precipitation of the aluminium and iron oxides with ammonia.

[3] F. Taboury, *Compt. rend.*, **159**, 180, 1914; H. Thurnwald and A. A. Benedetti-Pichler (*l.c.*); I. M. Kolthoff and E. B. Sandell (*l.c.*).

[4] Manganese, if present, is liable to be partially precipitated with the beryllia. The amount can be determined colorimetrically and deducted—F. G. Hills (*l.c.*).

[5] When much iron is present, H. Fischer and G. Leopoldi (*l.c.*) recommend its removal by Rothe's ether extraction process (page 505). See H. V. Churchill, R. W. Bridges and M. F. Lee (*l.c.*) for the removal of the bulk of the aluminium in the determination of beryllium in aluminium metal, *via* Haven's process (*v. infra*).

[6] G. Wyrouboff (*Bull. Soc. chim.*, (3), **27**, 733, 1902; *Chem. News*, **86**, 67, 1902) makes use of the sparing solubility of beryllium oxalate and the relative solubility of the corresponding aluminium, ferric and chromium salts. F. S. Havens (*Amer. J. Sci.*, (4), **4**, 111, 1897; **6**, 45, 1898; *Zeit. anorg. Chem.*, **16**, 15, 1898; **18**, 147, 1898) saturates a solution of the mixed chlorides and an equal volume of ether with hydrogen chloride. The ferric chloride dissolves in the ether and the aluminium chloride is precipitated. For a process based on the solubility of beryllium nitrate in amyl alcohol, see P. E. Browning and S. B. Kuzirian, *8th Inter. Congress App. Chem.*, **1**, 87, 1912. For a separation *via* acetyl chloride in acetone, see H. D.

Minnig, *Amer. J. Sci.*, (4), **40**, 482, 1915. A. Kling and E. Gmelin (*Bull. Soc. chim.*, (4), **15**, 205, 1914) sublime basic beryllium acetate under reduced pressure from a mixture of aluminium and ferric acetates. P. Adami (*Ann. Chim. applicata*, **23**, 428, 1933) uses a similar method with a mixture of formates. For the volumetric determination of beryllium with quinalizarin, see H. Fischer, *Wiss. Veröff. Siemens-Konz.*, **5**, 99, 1926; **8**, 9, 1929; *Zeit. anal. Chem.*, **73**, 54, 1928. Compare B. S. Evans, *Analyst*, **60**, 291, 1935. For the use of tannin as a precipitating agent for beryllium, see L. Moser and M. Niessner, *Monats.*, **48**, 113, 1927; L. Moser and J. Singer, *ib.*, **48**, 673, 1927; W. R. Schoeller and H. W. Webb, *Analyst*, **61**, 235, 1936; for hydrazine carbonate, A. Jilek and J. Kota, *Coll. Czech. Chem. Comm.*, **2**, 571, 1930; for guanidine carbonate, A. Jilek and J. Kota, *ib.*, **3**, 336, 1931; *Zeit. anal. Chem.*, **89**, 345, 1932; for selenic acid, J. Kota, *Chem. Listy*, **27**, 79, 100, 128, 150, 194, 1933. For the determination of beryllium in the presence of fluorine, see V. M. Zvenigorodskaya and A. A. Gaigerova, *Zeit. anal. Chem.*, **97**, 327, 1934. For the use of calcium ferrocyanide which, in dilute solutions, precipitates aluminium but not beryllium, see T. G. y Arnal, *Anal. Fis. Quim.*, **32**, 868, 1934. For the separation of beryllium from the alkaline earths, see L. Moser and F. List, *Monats.*, **50**, 181, 1929. For summaries and criticisms of methods, see H. T. S. Britton, *Analyst*, **46**, 359, 437, 1921; **47**, 50, 1922; L. Fresenius and M. Frommes, *Zeit. anal. Chem.*, **87**, 273, 1932; **93**, 275, 1933; J. Dewar and P. A. Gardiner, *Analyst*, **61**, 536, 1936; T. Akiyama, *Journ. Pharm. Soc. Japan*, **56**, 893, 1936; **57**, 19, 1937; T. Akiyama and Y. Mine, *ib.*, **56**, 885, 1936; **57**, 17, 1937; H. S. Miller, *Ind. Eng. Chem. Anal. Ed.*, **9**, 221, 1937. For the spectrographic detection and determination of beryllium in rocks and minerals, see W. Kemula and J. Rygielski, *Przemysl Chem.*, **17**, 89, 1933.

CHAPTER XXXIII.

SPECIAL METHODS FOR IRON COMPOUNDS.

"When Nature takes up the brush, iron is almost always on the palette."—R. J. HAÜY.

§ 245. The Volumetric Determination of Iron in Hydrochloric Acid Solutions—Reinhardt's Process.

IRON compounds are so common as components of colours, and the effects of iron are so important in the silicate industries, that it is necessary to indicate some alternative methods of analysis other than those described on pages 169 *et seq.* It has been shown that the permanganate titration is useless in the presence of organic matter,[1] and of much hydrochloric acid, unless special precautions be taken—in the latter case, because of the disturbing effects of a side reaction, probably indicated by the equation:

$$16HCl + 2KMnO_4 = 4Cl_2 + 2MnCl_3 + 2KCl + 8H_2O$$

The acid acts as a reducing agent and furnishes high results (page 177). This effect was pointed out by Löwenthal and Lenssen[2] in 1862. Kessler[3] showed that the presence of manganese sulphate inhibits the side reaction; and Zimmermann[4] further proved that satisfactory results can be obtained in the presence of hydrochloric acid, provided sufficient manganese sulphate be present.

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[1] Ferric salts in the presence of organic matter may be treated by adding a little copper sulphate as catalytic agent and titrating the solution with standard thiosulphate until a drop gives no red coloration with ammonium thiocyanate—J. T. Hewitt and G. R. Mann, *Analyst*, **37**, 179, 1912.

[2] J. Löwenthal and E. Lenssen, *Pogg. Ann.*, **118**, 41, 1863; **119**, 225, 1863; *Zeit. anal. Chem.*, **1**, 329, 1862; E. Lenssen, *ib.*, **2**, 169, 1863; R. Fresenius, *ib.*, **1**, 361, 1862; H. Kinder, *Stahl Eisen*, **27**, 344, 1907; **28**, 508, 1908; P. Lehnering, *ib.*, **27**, 202, 601, 1907; A. Müller, *ib.*, **26**, 147, 1906; **27**, 204, 1907; H. Wdowiszewski, *Zeit. anal. Chem.*, **42**, 183, 1903; H. Weber, *ib.*, **46**, 788, 1907; **47**, 249, 1908; J. Brown, *Chem. News*, **93**, 59, 1906; *Amer. J. Science*, (4), **19**, 31, 1905.

[3] F. Kessler, *Pogg. Ann.*, **118**, 17, 1863; **119**, 218, 1863; *Zeit. anal. Chem.*, **2**, 280, 1863; **21**, 219, 1882.

[4] C. Zimmermann, *Ber.*, **14**, 779, 1881; *Liebig's Ann.*, **213**, 305, 1882; H. P. Cady and A. P. Ruediger, *Journ. Amer. Chem. Soc.*, **19**, 575, 1897 (HgSO₄); C. T. Hood, *Chem. News*, **50**, 278, 1884 (MgSO₄); J. Krutwig and A. Cocheteux, *Ber.*, **16**, 1534, 1883; *Chem. News*, **48**, 102, 1883; N. W. Thomas, *Amer. Chem. Journ.*, **4**, 359, 1882; O. L. Barnebey, *Journ. Amer. Chem. Soc.*, **36**, 1429, 1914; **37**, 1481, 1915; L. Szegö, *Giorn. Chim. Ind. Appl.*, **14**, 226, 1932. H. Rose (*Handbuch der analytischen Chemie*, Braunschweig, **2**, 926, 1871) says that potassium fluoride and potassium sulphate inhibit the reaction; O. Follenius (*Zeit. anal. Chem.*, **11**, 177, 1872) denies this. O. L. Barnebey (*Journ. Amer. Chem. Soc.*, **37**, 1481, 1915) says that the end-point is unstable in the presence of hydrofluoric acid and recommends the addition of boric acid to the solution before titration. For the alleged efficacy of colloidal silicic acid in inhibiting the reaction between permanganate and hydrochloric acid, see R. Schwarz and B. Rolfes, *Chem. Ztg.*, **43**, 51, 1919; E. Dittler, *ib.*, **43**, 262, 1919; R. Schwarz, *ib.*, **43**, 499, 1919; **44**, 310, 1920. The claim was refuted by L. Brandt, *Chem. Ztg.*, **43**, 373, 394, 1919; **44**, 101, 121, 1920; *Zeit. anal. Chem.*, **62**, 417, 1923.

Action of Manganous Sulphate.— According to Manchot,[1] the first action of the permanganate in the titration of a ferrous salt is to form what he calls a "primary oxide"—probably Fe_2O_5. In symbols:

$$Mn_2O_7 + 2FeO = Fe_2O_5 + 2MnO_2$$

The manganese dioxide so formed oxidises a further quantity of the ferrous salt to the ferric state. In symbols:

$$MnO_2 + 2FeO = Fe_2O_3 + MnO$$

In the presence of a sufficient amount of manganous salt, the ferric "primary oxide"—Fe_2O_5—oxidises the manganous oxide—MnO—back to MnO_2:

$$Fe_2O_5 + 2MnO = Fe_2O_3 + 2MnO_2$$

On the other hand, if but little manganous oxide be present in the solution, and hydrochloric acid is also present, the latter is oxidised by the "primary oxide." In symbols:

$$Fe_2O_5 + 10HCl = 2FeCl_3 + 5H_2O + 2Cl_2$$

"According to this theory," says Manchot,[2] "the manganese salt acts in two ways. In the first place, it modifies the velocity of the reaction between the ferrous oxide and the permanganate; since, according to Volhard, the permanganate first reacts with the manganese salt to form manganese peroxide, which, in turn, reacts with the ferrous salt. In the second place, the manganous salt 'carries' oxygen from the ferric 'primary oxide'—Fe_2O_5—and gives it up to the unoxidised ferrous salt. In both cases it is essential that the manganese peroxide shall not react rapidly with the hydrochloric acid, and that the quantity of manganous salt shall not exceed the amount of iron present in the solution." Whatever be the right explanation of the action, the ill effects of the hydrochloric acid are counteracted when a manganous salt is present in suitable proportions, and the amount of hydrochloric acid is not too great.

The Action of Phosphoric Acid.—The presence of ferric chloride in the solution interferes with the end-point, on account of the yellow colour of this salt which is formed during the titration. This difficulty was overcome by Reinhardt,[3] who showed that in the presence of phosphoric acid the solution remains colourless until the pink colour of the permanganate appears. This is probably due to the formation of a colourless iron phosphate.

Some contradictory statements have been published as to the efficiency of the subjoined Reinhardt's method [4] of conducting the permanganate titration in the presence of hydrochloric acid, but it can be made to give results as con-

[1] W. Manchot, *Liebig's Ann.*, **325**, 105, 1902; J. Volhard, *ib.*, **198**, 337, 1879; A. Skrabal, *Zeit. anal. Chem.*, **42**, 359, 1903. Compare II. Bassett and I. Sanderson, *Journ. Chem. Soc.*, 207, 1936.

[2] For the theory of induced reactions, see J. W. Mellor, *Chemical Statics and Dynamics*, London, 315, 333, 1904.

[3] C. Reinhardt, *Stahl Eisen*, **4**, 704, 1889; *Chem. Ztg.*, **13**, 323, 1889; *Zeit. anal. Chem.*, **36**, 794, 1897; H. Weber, *ib.*, **53**, 444, 1914; Report, *Zeit. angew. Chem.*, **24**, 1118, 1913; G. J. Hough, *Journ. Amer. Chem. Soc.*, **32**, 545, 1910.

[4] L. Brandt, *Chem. Ztg.*, **32**, 812, 830, 840, 851, 1908; *Zeit. anal. Chem.*, **53**, 729, 1914; C. T. Mixter and H. W. Dubois, *Journ. Amer. Chem. Soc.*, **17**, 405, 1895; G. P. Baxter and J. E. Zanetti, *Amer. Chem. Journ.*, **33**, 500, 1904; G. P. Baxter and H. L. Frevert, *ib.*, **34**, 109, 1905; F. W. Harrison and F. M. Perkin, *Analyst*, **33**, 47, 1908; G. C. Jones and J. H. Jeffery, *ib.*, **34**, 304, 1909; J. A. N. Friend, *Journ. Chem. Soc.*, **95**, 1228, 1909; W. C. Birch, *Chem. News*, **99**, 61, 73, 1909; F. A. Gooch and C. A. Peters, *ib.*, **80**, 78, 91, 1899; *Amer. J. Science*, (4), **7**, 461, 1899; M. Wunder and A. Stoicoff, *Ann. Chim. anal.*, **17**, 361, 1912; E. Hintz, *Zeit. angew. Chem.*, **27**, 9, 1914; H. P. Cady and A. P. Rüdiger, *Journ. Amer. Chem. Soc.*, **19**, 575, 1897; M. Hauffe, *Chem. Ztg.*, **21**, 894, 1897.

sistent as the best volumetric methods, provided a uniform and favourable pro-
cedure be adopted. In rapid routine work, where the titanic oxide is neglected,[1]
the solution obtained after filtering off the silica may be divided into two equal
portions—say 100 c.c. each. In one, the iron and alumina are precipitated in
the usual manner; in the other portion, the iron can be determined by the
permanganate titration as follows:—

The Reduction of Ferric Salts by Stannous Chloride.[2]—The amount of hydro-
chloric acid in the 100 c.c. under investigation should not exceed 4N-HCl.
Heat the solution to boiling, add a solution of stannous chloride[3] gradually,
drop by drop, with constant stirring, until all the ferric chloride is reduced to
ferrous chloride.[4] It is important to add as little stannous chloride as possible
in excess of that required to reduce the iron.[5] The difficulties incidental to this
method of reduction are: (1) the danger of adding insufficient stannous
chloride; and (2) the tendency to add too much. If much iron be present, the
colour is a fair guide when the reduction is nearly complete; but when the
colour is very faint, the stannous chloride is added until a drop of the solution
brought quickly into contact with a drop of ammonium thiocyanate solution on
a white tile gives no red coloration.[6] When the solution is cold, add rapidly
5 c.c. of a solution of mercuric chloride[7] in order to destroy the excess of
stannous chloride. If no precipitate forms, sufficient stannous chloride was
not added and some ferric chloride has not been reduced; if a grey precipitate
forms, too much stannous chloride was added. This precipitate reacts with
the permanganate, spoiling the titration. If only a white precipitate of
mercurous chloride is formed, it will do no harm[8] and the solution, after
standing 10 minutes, is ready for titration.

The Titration with Potassium Permanganate.—Wash the ferrous chloride
solution into a 600 c.c. beaker, containing a mixture of 25 c.c. of Reinhardt's

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[1] If titanium is to be determined, reserve an aliquot portion of the solution for that
purpose.

[2] C. F. Mohr, *Liebig's Ann.*, 113, 257, 1860. For the rate of reduction of ferric chloride
by stannous chloride, see L. Kahlenberg, *Journ. Amer. Chem. Soc.*, 16, 314, 1894; A. A.
Noyes, *Zeit. phys. Chem.*, 16, 546, 1895; 21, 16, 1896. Ferric chloride solutions can be reduced
by amalgamated zinc in the presence of manganous sulphate—D. L. Randall, *Zeit. anorg.
Chem.*, 48, 389, 1906.

[3] STANNOUS CHLORIDE SOLUTION.—Dissolve 21 grms. of crystalline $SnCl_2.2H_2O$ in 330 c.c.
of concentrated hydrochloric acid and make the solution up to a litre with water. Add
granulated tin and boil the solution until it is clear and colourless. Preserve the solution
in a well-stoppered bottle. Some keep a stick of metallic tin in the stoppered bottle with
the stock solution. 1 c.c. of the stannous chloride solution will reduce about 0·03 grm.
of ferric chloride.

[4] Titanium chloride is not reduced by stannous chloride in hot or cold solutions and
hence the iron determination is not affected by the presence of titanium.

[5] W. F. Stock and W. E. Jack, *Chem. News*, 31, 63, 1875; 30, 221, 1874; R. G. Durrant,
Journ. Chem. Soc., 107, 623, 1915.

[6] If the material under analysis has been opened up by fusion in a platinum crucible,
traces of platinum may pass into solution. On subsequent reduction with stannous chloride,
the solution will turn yellow. Hence it is impossible to gauge when the ferric salt has all
just been reduced. In such circumstances the platinum must be removed from the solution
by hydrogen sulphide prior to reduction and the excess of the hydrogen sulphide boiled off.
Cf. O. Rothe and A. P. Sobrinho, *Rev. Brasil Chim.*, 1, 129, 1929; R. W. Mahon, *Amer.
Chem. Journ.*, 15, 578, 1893.

[7] MERCURIC CHLORIDE SOLUTION.—A saturated solution contains about 56 grms. per
litre at 15°. 1 c.c. of the mercuric chloride will oxidise 1·2 c.c. of the stannous chloride
solution.

[8] The mercurous chloride is not affected by potassium dichromate (Kessler), nor by
potassium permanganate (Reinhardt). For the action of mercurous chloride on ferric salts
($HgCl + FeCl_3 = HgCl_2 + FeCl_2$) see C. Meineke, *Zeit. öffent. Chem.*, 4, 433, 1898. Hence the
titration should be quickly done, to prevent the mercurous salt standing in contact with the
ferric salt longer than is necessary—A. E. Haswell, *Rep. anal. Chem.*, 2, 841, 1882.

solution [1] with about 300 c.c. of distilled water and one drop of the solution of permanganate.[2] Titrate the solution at once with permanganate, which is added gradually, drop by drop, with constant stirring. The calculations are made as indicated on page 180. The whole determination occupies about 20 or 30 minutes.[3] Amounts of copper less than 0·01 per cent. may be neglected in ordinary technical analysis. If more than this amount be present, the copper should be removed.[4]

§ 246. The Volumetric Determination of Iron—Penny's Dichromate Process.

Instead of titrating for iron, in hydrochloric acid solutions, with potassium permanganate according to Reinhardt's process, Penny's dichromate process [5] is commonly used. The ferrous salt is here oxidised with potassium dichromate instead of potassium permanganate. The presence of hydrochloric acid [6] does no particular harm, although the end-point is a little sharper with sulphuric than with hydrochloric acid. The end-point is not so easily determined when potassium ferricyanide is used as an external indicator, and it is easy to overtitrate. However, the use of potassium ferricyanide has been largely superseded by that of internal organic indicators, especially diphenylamine sulphate. Details for the use of both types of indicator are given here.

Potassium Ferricyanide Indicator.—Dissolve 4·904 grms. of fused potassium dichromate [7] in a litre of water. Standardise this solution by dissolving 39·2132 grms. of Mohr's salt in 10 per cent. sulphuric acid and making up to a litre. Pipette 25 c.c. of this solution into a beaker, and charge the burette with the solution of potassium dichromate. Place 10 or 12 drops of a freshly prepared solution of potassium ferricyanide [8] (1 : 100) separately as spots on a white tile.[9] At intervals during the titration, remove a drop of the solution

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[1] REINHARDT'S SOLUTION.—Dissolve 200 grms. of crystalline manganese sulphate in 1000 c.c. of water; add to this a cold mixture of 400 c.c. of concentrated sulphuric acid (sp. gr. 1·8), 600 c.c. of water, and 1000 c.c. of phosphoric acid (sp. gr. 1·3).

[2] To oxidise traces of organic matter in the water.

[3] For the use of potassium bromide in iron-permanganate titrations in the presence of hydrochloric acid, see R. Meurice, *Ann. Chim. anal.*, (2), **3**, 23, 1921; W. Manchot and F. Oberhauser, *Zeit. anorg. Chem.*, **138**, 189, 1924.

[4] K. Schröder, *Zeit. öffent. Chem.*, **14**, 477, 1908.

[5] F. Penny, *Chem. Gaz.*, **8**, 330, 1850; *L'Institut*, **18**, 27, 1850; J. Schabus, *Sitzber. Akad. Wiss. Wien.*, **6**, 397, 1851; F. Kessler, *Zeit. anal. Chem.*, **11**, 249, 1872.

[6] Organic matter decomposes hot or cold solutions as in the case of permanganate, but potassium dichromate is not so much affected as the permanganate. See page 178.

[7] POTASSIUM DICHROMATE SOLUTION.—Fuse about 5 grms. of the pure crystallised salt in a platinum crucible below a red heat. The salt melts in the neighbourhood of 400°. Cool in a desiccator. The fusion must not be made at too high a temperature. R. W. Atkinson (*Chem. News*, **49**, 117, 1884) states that, "however carefully the heat be regulated, on dissolving in water, and allowing to settle, a green deposit of chromic oxide will be found at the bottom of the flask or beaker. This shows that a small amount of decomposition occurs during the fusion, and that the value of the standard must be lower than is theoretically required for the amount of dichromate weighed out." For the use of potassium dichromate as a standard in volumetric work, see G. Bruhns, *Journ. prakt. Chem.*, (2), **93**, 73, 312, 1916; (2), **95**, 37, 1917.

[8] The ferricyanide should be free from ferrocyanide, which gives a blue coloration with ferric salts. It is advisable to rinse a crystal of the ferricyanide first with dilute nitric acid and then several times with water before dissolving it up. For the disturbing effects of copper, see J. S. Parker, *Chem. News*, **22**, 313, 1870. Potassium ferricyanide will show 1 part of iron in 500,000 parts of water—A. Wagner, *Zeit. anal. Chem.*, **20**, 349, 1881.

[9] Some prefer a slab of paraffin wax, or a white tile covered with a layer of the same, owing to the form the drops take on the wax, and the ease in cleaning the waxed slab. R. Seligmann and F. J. Willott, *Journ. Soc. Chem. Ind.*, **24**, 1278, 1905.

undergoing titration on a clean glass rod and mix it with one of the drops on the tile—"spot test." A blue coloration shows that the reaction is not complete and that the solution still contains ferrous iron. When a drop of the solution gives no sign of a blue coloration, the titration is complete. If a drop of the solution under titration be touched against the side of a drop of the potassium ferricyanide, a little practice will enable one to judge when the end of the reaction is near.[1] The reaction is represented by the equation:

$$6FeCl_2 + K_2Cr_2O_7 + 14HCl = 6FeCl_3 + 2CrCl_3 + 2KCl + 7H_2O$$

Zinc is objectionable as a reducing agent for the dichromate titrations, because the zinc ferricyanide formed in the "spot test" interferes with the indicator. Reductions for the dichromate titration are usually made with stannous chloride (page 500). The solution reduced with stannous chloride is titrated with the standard dichromate as indicated above. The calculation is obvious.[2]

Diphenylamine Sulphate Indicator.[3]—After reduction with stannous chloride, add to the solution 15 c.c. of sulphuric-phosphoric acid mixture [4] and three drops of diphenylamine sulphate solution.[5] Dilute to 150–200 c.c. and titrate with a standard solution of potassium dichromate until a green colour appears. Now add the dichromate drop by drop, waiting after each addition. The colour changes to blue-green or greyish-blue, if much iron be present, and at the end-point an intense violet colour develops. The indicator change is reversible, hence if the end-point has been overshot, a definite volume of the reduced iron solution can be added and the titration completed. The results by this method are excellent.[6] No fading end-point is given as in permanganate titrations in the presence of mercurous chloride. Aluminium, chromium, nickel, cobalt, manganese and zinc do not interfere, neither do organic sub-

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[1] The development of the ferricyanide "blue" is slow with dilute solutions of ferrous salts, and the end-point may thus be judged prematurely. To get the true end of the reaction, let the mixed drop stand 5 minutes covered with a crucible lid to shut out the light. The reaction is disturbed by elements which form insoluble ferricyanides—the brown colour with manganese, nickel or copper, for instance, masks the reaction with dilute ferrous solutions. Hence the ferricyanide is generally made slightly "acid" to prevent the formation of insoluble ferricyanides. H. Vogel (*Chem. News*, **23**, 142, 1871; R. W. Atkinson, *ib.*, **49**, 217, 1884; L. van Itallie, *Pharm. Weekblad*, **40**, 490, 1903) says that 30 seconds' exposure to sunlight is sufficient to make potassium ferricyanide solutions give a blue colour with ferric salts.

[2] For titrating ferric chloride solutions directly with stannous chloride, see page 316, where the converse process is described. For the titration of ferric salts with stannous chloride using methylene blue as indicator, see C. Russo, *Gazz. Chim. Ital.*, **44**, i, 1, 1914; H. Uelsmann, *Zeit. anal. Chem.*, **16**, 50, 1877; R. W. Mahon, *Amer. Chem. Journ.*, **15**, 360, 1893. For cobalt chloride or cobalt nitrate indicators, see F. P. Venable, *Journ. Anal. App. Chem.*, **1**, 312, 1887; A. C. Campbell, *ib.*, **2**, 4, 1888; F. H. Morgan, *ib.*, **2**, 172, 1888.

[3] J. Knop, *Journ. Amer. Chem. Soc.*, **46**, 263, 1924; W. W. Scott, *Standard Methods of Chemical Analysis*, New York, 255, 1927; F. J. Watson, *Chem. Eng. Min. Rev.*, **22**, 355, 1928; L. Szebellédy, *Zeit. anal. Chem.*, **81**, 97, 1930; C. B. Core, *Chemist-Analyst*, **20**, 14, 1931; R. P. Hudson, *ib.*, **20**, 6, 1931; W. K. Gibson, *ib.*, **26**, 29, 1937; C. J. Schollenberger, *Journ. Amer. Chem. Soc.*, **53**, 88, 1931; O. Rothe and A. P. Sobrinho, *Rev. Brasil Chim.*, **1**, 129, 1929; C. T. Bennett and N. R. Campbell, *Quart. Journ. Pharm. Pharmacol.*, **6**, 436, 1933. W. W. Scott (*Journ. Amer. Chem. Soc.*, **46**, 1396, 1924) says that ferrous iron solutions containing hydrochloric acid can be satisfactorily titrated by this method with permanganate.

[4] SULPHURIC-PHOSPHORIC ACID MIXTURE.—Dilute 150 c.c. of sulphuric acid (sp. gr. 1·84) and 150 c.c. of phosphoric acid (sp. gr. 1·7) to 1000 c.c.

[5] DIPHENYLAMINE SULPHATE SOLUTION.—Dissolve 1 grm. of pure diphenylamine, $(C_6H_5)_2NH$, in 100 c.c. of concentrated sulphuric acid. The solution darkens on standing, but this does no harm. H. M. State (*Ind. Eng. Chem. Anal. Ed.*, **8**, 259, 1936) melts the diphenylamine to a clear liquid, adds the required amount of sulphuric acid and mixes by shaking.

[6] Occasional failures have, however, been reported—I. M. Kolthoff and L. A. Sarver, *Elektrochem. Zeit.*, **36**, 139, 1930.

stances. Copper in excess of 1 mgrm. leads to low results, as it apparently catalyses the atmospheric oxidation of the ferrous iron. As arsenic is oxidised by dichromate from the arsenious to the arsenic state, it must be removed prior to titration.[1]

§ 247. The Gravimetric Determination of Iron—Ilinsky and Knorre's α-Nitroso-β-naphthol Process.

Several methods are available for the gravimetric precipitation of iron in the presence of aluminium salts.[2] Ilinsky and Knorre's process [3] gives satisfactory results in separating ferric or ferrous iron from aluminium, chromium, manganese, nickel, zirconium, zinc, lead, cadmium, antimony, arsenic, magnesium, calcium, beryllium, but not vanadium, tungsten, copper and cobalt. Silver, tin, bismuth, as well as molybdenum, interfere with the precipitation of iron, cobalt, vanadium, tungsten and copper by the α-nitroso-β-naphthol process. Some phosphorus, if this element be present, will be precipitated with the iron.[4] The following is the method: —

The solution of the chloride or sulphate after oxidation, if necessary, is first neutralised with sodium carbonate and then acidified with a few drops of hydrochloric acid. The cold solution is stirred with a concentrated acetic acid solution of α-nitroso-β-naphthol.[5] A voluminous precipitate of

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[1] For the use of *s*-diphenylcarbazide, CO(NH.NH.C₆H₅)₂, as an internal indicator, see P. Cazeneuve, *Chem. Ztg.*, **24**, 684, 1900; *Bull. Soc. chim.*, (4), **23**, 592, 701, 769, 1900; L. Brandt, *Zeit. anal. Chem.*, **45**, 95, 1906; **53**, 1, 1914; **53**, 729, 1914; O. L. Barnebey and S. R. Wilson, *Journ. Amer. Chem. Soc.*, **35**, 156, 1913. For *p*-phenetidine, C₂H₅O.C₆H₄.NH₂, L. Szebellédy, *Zeit. anal. Chem.*, **81**, 97, 1930; *Magyar Chem. Fol.*, **36**, 40, 1930; *Chem. Zentr.*, (2), 274, 1930. For bi-o-anisidine, M. E. Weeks, *Ind. Eng. Chem. Anal. Ed.*, **4**, 127, 1932; H. E. Crossley, *Analyst*, **61**, 164, 1936. For o-phenanthroline. G. H. Walden, junr., L. P. Hammett and R. P. Chapman, *Journ. Amer. Chem. Soc.*, **55**, 2649, 1933; H. H. Willard and P. Young, *Ind. Eng. Chem. Anal. Ed.*, **7**, 57, 1935. For naphthidine, L. E. Straka and R. E. Oesper, *ib.*, **6**, 465, 1934; compare S. Cohen and R. E. Oesper, *ib.*, **8**, 364, 1936.

[2] Trimethylamine precipitates iron in the presence of aluminium and chromium compounds—L. Vignon, *Journ. Pharm. Chim.*, (5), **12**, 677, 1885; *Zeit. anal. Chem.*, **26**, 631, 1887. A solution of naphthenic acid in benzene precipitates ferrous oxide in the presence of aluminium, K. Charitschkoff, *Chem. Ztg.*, **35**, 463, 671, 1911; E. Pyhälä, *ib.*, **36**, 869, 1912; I. I. Lutshinnskii, *ib.*, **35**, 1204, 1911. Pyridine also precipitates iron in the presence of manganese, nickel and cobalt—R. B. Moore and I. Miller, *Journ. Amer. Chem. Soc.*, **30**, 593, 1908; *Chem. News*, **98**, 105, 1908—and J. A. Sanchez (*Bull. Soc. chim.*, (4), **9**, 880, 1911; N. Conta, *Roma, Rend. Soc. Chim. Ital.*, (2), **4**, 256, 1912; *Chem. Ztg.*, **36**, 1363, 1912) recommends the pyridine precipitation for separating iron and manganese. Zinc should be absent, for it is precipitated by pyridine. For the separation of iron, aluminium, chromium and titanium from nickel, cobalt, manganese and zinc by hexamethylenetetramine, see C. Kollo, *Bul. Soc. Chim. România*, **2**, 89, 1920; P. Rây and A. K. Chattopadhya, *Zeit. anorg. Chem.*, **169**, 99, 1928; P. Rây, *Zeit. anal. Chem.*, **86**, 13, 1931; L. Lehrman, E. A. Kabat and H. Weisberg, *Journ. Amer. Chem. Soc.*, **55**, 3509, 1933; F. Allen, H. Weiland and H. Loofman, *Angew. Chem.*, **46**, 668, 1933. Hydrazine hydrate also precipitates ferric iron quantitatively—E. Schirm, *Chem. Ztg.*, **35**, 897, 1911; A. Jílek and V. Vicovsky, *Coll. Czech. Chem. Comm.*, **3**, 379, 1931.

[3] M. von Ilinsky and G. von Knorre, *Ber.*, **18**, 2728, 1885; G. von Knorre, *Zeit. anal. Chem.*, **28**, 234, 1889; *Zeit. angew. Chem.*, **6**, 264, 1893; **17**, 641, 1904; R. Burgass, *ib.*, **9**, 596, 1896; L. L. de Koninck, *Rev. Univ. Mines*, (2), **9**, 243, 1890; M. Schleier, *Chem. Ztg.*, **16**, 420, 1892; M. Béard, *Ann. Chim. anal.*, **10**, 41, 1905; E. A. Atkinson and E. F. Smith, *Journ. Amer. Chem. Soc.*, **17**, 688, 1895; G. Svedenius, *Acta paediatr.*, **9**, 1, 1929; *Chem. Zentr.*, (2), 323, 1931.

[4] Phosphorus interferes with most of the gravimetric processes for iron, and in the presence of phosphorus a volumetric process is preferable—C. E. Corfield and W. R. Pratt, *Pharm. Journ.*, **93**, 131, 1914.

[5] α-Nitroso-β-naphthol Solution.—8 grms. of α-nitroso-β-naphthol are dissolved in 300 c.c. of glacial acetic acid. The solution is diluted with 300 c.c. of water, and filtered. The solution will keep about a month in a dark place.

$Fe(C_{10}H_6O.NO)_3$ separates on standing, say, overnight. Try if any more reagent causes any further precipitation in the clear solution. Wash the precipitate with 50 per cent. acetic acid and finally with cold water.[1] The precipitate is dried and ignited in a capacious crucible,[2] heating so that the temperature gradually rises. When all the carbon has burned off, the crucible is cooled and the weight of Fe_2O_3 determined. Trial results on known mixtures of aluminium and iron are quite good. If necessary, the organic matter in the filtrate is subsequently destroyed by boiling with hydrochloric acid and potassium chlorate.

§ 248. The Gravimetric Determination of Iron — Baudisch's "Cupferron" Process.

Baudisch[3] has shown that ammonium nitrosophenylhydroxylamine, $C_6H_5N(NO)ONH_4$—called for brevity "cupferron" or Baudisch's reagent—promises to be a valuable agent for separating ferric and cupric salts from most other metals—mercury, vanadium, tin, lead, bismuth, silver, cerium, tungsten, uranium and silica, however, may be wholly or partially precipitated with the iron and copper if these elements be present. Excessive amounts of phosphorus, alkalies and alkaline earths interfere with the separations; titanium and zirconium are precipitated with the iron.[4] The precipitated iron and copper salts are but slowly attacked by 2N-HCl in the cold; but they are decomposed by hot acid. Cold dilute sodium carbonate has no appreciable action, but the alkali hydroxides decompose the precipitate rapidly. Ammonia does not affect the iron salt, but it quickly dissolves the copper salt, and it is therefore possible to separate the iron and copper salts by digesting the mixed salts with ammonia in the cold. The precipitation is best made in strongly acid (hydrochloric, sulphuric or acetic[5]) solutions, thus:—

Add 20 c.c. of concentrated hydrochloric acid to 100 c.c. of solution at the room temperature. Add a cold solution of Baudisch's reagent[6] slowly, with constant stirring. A reddish-brown (iron)—or greyish-white (copper)—flocculent precipitate separates. The end of the precipitation is easy to

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[1] There is no particular difficulty in washing the precipitate, except its comparatively large volume.

[2] Capacious, because the precipitate swells very much during the earlier stages of the ignition.

[3] O. Baudisch, *Chem. Ztg.*, **33**, 1298, 1909; **35**, 913, 1911; O. Baudisch and V. L. King, *Journ. Ind. Eng. Chem.*, **3**, 629, 1911; H. Biltz and O. Hödtke, *Zeit. anorg. Chem.*, **66**, 426, 1910; J. Hanuš and A. Soukup, *ib.*, **68**, 52, 1910; R. Fresenius, *Zeit. anal. Chem.*, **50**, 35, 1911; H. Nissenson, *Zeit. angew. Chem.*, **23**, 969, 1910; J. Bellucci and L. Grassi, *Gazz. Chim. Ital.*, **43**, i, 570, 1913; F. Ferrari, *Ann. Chim. appl.*, **4**, 341, 1915; G. E. F. Lundell and H. B. Knowles, *Journ. Ind. Eng. Chem.*, **12**, 344, 1920.

[4] J. Brown, *Journ. Amer. Chem. Soc.*, **39**, 2358, 1917.

[5] Acetic acid is best for copper. G. E. F. Lundell (*Journ. Amer. Chem. Soc.*, **43**, 847, 1921) says that the process is quantitative in solutions containing as much as 20 per cent. free sulphuric or hydrochloric acid and that the precipitate is not dissolved by cold, dilute (1 in 9) hydrochloric acid wash liquor. Conversely, E. H. Archibald and R. V. Fulton (*Trans. Roy. Soc. Canada*, **13**, (3), 243, 1919) assert that the iron precipitate is slightly soluble in the acid solution from which it is precipitated and also in the wash water. They recommend the addition of ammonium chloride, before precipitation, to reduce the solubility. For the solubilities of metallic derivatives of cupferron in various media, see A. Pinkus and F. Martin, *Chim. et Ind.*, Special No., 182, 1927; *Journ. Chim. phys.*, **24**, 83, 1927.

[6] BAUDISCH'S CUPFERRON REAGENT.—Dissolve 5 grms. of the white crystalline solid—ammonium nitrosophenylhydroxylamine—in water and make the solution up to 100 c.c. The solution will keep in the dark for about a week. If exposed to the light, it becomes turbid owing to the formation of nitrobenzene. Old turbid solutions should be filtered before

recognise, since small white crystals of nitrosophenylhydroxylamine separate as soon as all the copper or iron has been precipitated. It is then necessary to add a further excess of the reagent, say, one-fifth of the volume of that already added. After a few minutes, filter by suction on a paper filter. If the precipitate creeps through the paper, re-filter or stand in the cold and then re-filter. Wash first with 2N-HCl, containing a few drops of the reagent solution, and then with 5N-ammonia[1] in the case of iron, or sodium carbonate in the case of copper, so as to remove the excess of the reagent. In the latter case finish the washing with water. The precipitate can be ignited very slowly in the ordinary way and weighed as oxide—Fe_2O_3 (or CuO).[2]

Trial separations of iron from aluminium, nickel and chromium, and of copper from zinc and cadmium, are excellent. The chief value of the process lies in the fact that it furnishes a useful means of precipitating iron in the presence of cobalt, zinc, manganese, nickel, chromium, aluminium, sulphates and moderate amounts of alkaline earths, alkalies and phosphates.[3] The separation of copper from cadmium and zinc by this process offers, as yet, no particular advantages over the older process (page 365). It has also been recommended for separating titanium and zirconium from aluminium.[4]

§ 249. The Separation of Iron—Ether Process.

When a solution of ferric chloride with arsenic, antimony, aluminium, titanium, zirconium, chromium, vanadium, manganese, uranium, cobalt, nickel, copper, calcium and magnesium chlorides is acidified with hydrochloric acid, and shaken with ether, the mixture separates into two layers—an ethereal solution of ferric chloride above, and an aqueous solution of the other chlorides below. The two layers can be separated in a suitable funnel. Some gold, tungsten and molybdenum,[5] if present, are more or less completely removed with the iron in the ethereal layer. The same remark applies to thallium, stannous and mercuric chlorides.[6] W. Skey first proposed to separate iron from many associated elements in this manner; and he also suggested the corresponding separations: cobalt from nickel; and gold from platinum.[7]

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[1] Some analysts deprecate the use of ammoniacal wash liquors and say that losses, as shown by turbid filtrates, are occasioned thereby—G. E. F. Lundell, *Journ. Amer. Chem. Soc.*, 43, 847, 1921; A. Pinkus and F. Martin, *Chim. et Ind.*, Special No., 182, 1927.

[2] Finish the ignition over a Méker burner.

[3] For instance, say, 5 grms. of a brown iron ore are digested with 60 c.c. of concentrated hydrochloric acid and boiled with potassium chlorate. When cold, make the solution up to 500 c.c. Pipette 25 c.c. into a beaker, add 20 c.c. of hydrochloric acid and 100 c.c. of cold distilled water. Then precipitate the iron with cupferron as above.

[4] I. Bellucci and L. Grassi, *Atti R. Accad. Lincei*, (5), 22, i, 30, 1913; *Gazz. Chim. Ital.*, 43, i, 570, 1913; W. M. Thornton, junr., *Amer. Journ. Sci.*, (4), 37, 173, 407, 1914; W. M. Thornton, junr., and E. M. Hayden, junr., *ib.*, (4), 38, 137, 1914.

[5] Molybdenum appears to be but imperfectly separated in the absence of ferric chloride —W. Skey, *Chem. News*, 36, 48, 1877; 16, 201, 324, 1867; A. A. Blair, *Journ. Amer. Chem. Soc.*, 30, 1229, 1908; M. de Jong, *Zeit. anal. Chem.*, 41, 596, 1902; C. D. Braun, *ib.*, 2, 36, 1863; 6, 86, 1867. A. A. Blair (*l.c.*) says that the molybdenum is completely removed along with the ferric chloride by the ether and this enables molybdenum to be perfectly separated from vanadium, chromium, copper, manganese, nickel and aluminium in iron or steel.

[6] The chlorides of the alkalies, calcium, nickel, zinc and cadmium, and the thiocyanates of nickel, copper and zinc, are soluble in anhydrous but not in aqueous ether—W. Skey, *Chem. News*, 36, 48, 1877. Stannous chloride is soluble in ether—M. de Jong, *Zeit. anal. Chem.*, 41, 596, 1902.

[7] R. Willstätter (*Ber.*, 36, 1830, 1903) separates gold chloride from platinum chloride in aqueous solutions by extracting with ether—F. Mylius, *Zeit. anorg. Chem.*, 70, 203, 1911. See page 468.

Rothe,[1] however, has applied Skey's idea to the technical analysis of iron compounds and the method has now won a place in analytical practice. Two or three extractions with ether are sufficient to remove practically all the iron.

Effect of Acid.—The acidity of the solution requires attention.[2] If the

Table *LIV.—Relation between the Strength of the Acid and the Partition of Iron (as Ferric Chloride) between Ether and Dilute Acid.*

Strength of hydrochloric acid. (Sp. gr.)	Per cent. of iron.	
	Aqueous solution.	Ethereal solution.
1·193	99·0	1·0
1·164	97·5	2·5
1·158	92·84	7·16
1·151	74·0	26·0
1·123	7·2	92·8
1·115	2·4	97·6
1·111	2·0	98·0
1·105	1·95	98·05
1·103	1·95	98·05
1·091	3·3	96·7
1·0825	10·0	90·0
1·069	47·5	52·5
1·06	87·0	13·0
1·0525	98·4	1·6
1·0424	99·6	0·4

[1] J. W. Rothe, *Mitt. könig. tech. Ver.*, **10**, 132, 1892; *Chem. News*, 66, 182, 1892; *Stahl Eisen*, **12**, 1052, 1892; A. Ledebur, *ib.*, **13**, 333, 1893; E. Hanriot, *Bull. Soc. chim.*, (3), **7**, 161, 1892; F. N. Speller, *Chem. News*, **83**, 124, 1901; E. Pinerua, *ib.*, **75**, 193, 1897; A. A. Noyes, W. C. Bray and E. B. Spear, *Tech. Quart.*, **21**, 14, 1908; *Journ. Amer. Chem. Soc.*, **30**, 481, 1908; G. W. Sargent, *ib.*, **21**, 854, 1899; A. C. Langmuir, *ib.*, **22**, 102, 1900; H. Wedding, *Verhand. Ver. Bef. Gew.*, 84, 1893; S. Palkin, *Journ. Ind. Eng. Chem.*, **9**, 951, 1917; T. Szaffka, *Magyar Chem. Fol.*, **35**, 44, 1929; *Chem. Zentr.*, (2), 275, 1930; O. von Grossmann, *Chem. Ztg.*, **54**, 402, 1930; E. F. Kern, *Journ. Amer. Chem. Soc.*, **23**, 685, 1901 (separation of iron from uranium); J. M. Matthews, *ib.*, **20**, 846, 1898; *Chem. News*, **79**, 97, 112, 1899 (separation of iron from zirconium, thorium, cerium and titanium); F. A. Gooch and F. S. Havens, *ib.*, **74**, 296, 1896; *Amer. J. Science*, (4), **2**, 416, 1896 (separation iron and aluminium); A. Carnot, *Méthodes d'Analyse des Fontes des Fers et des Aciers*, Paris, 123, 1895. For the separation of iron and vanadium, E. Deiss and H. Leysaht, *Chem. Ztg.*, **35**, 878, 1911; for iron and nickel, J. P. Thompson, *Journ. Ind. Eng. Chem.*, **3**, 950, 1911; for iron and indium, L. M. Dennis and W. C. Geer, *Ber.*, **37**, 961, 1904; *Journ. Amer. Chem. Soc.*, **26**, 437, 1904; F. C. Mathers, *Ber.*, **40**, 1220, 1907; *Journ. Amer. Chem. Soc.*, **29**, 485, 1907; indium is slightly soluble in the ether, S. Palkin (*l.c.*); for iron and zinc, H. A. Bright, *Bur. Stand. Journ. Research*, **12**, 383, 1934. G. L. Norris (*Journ. Soc. Chem. Ind.*, **20**, 551, 1901) prefers a mixture of acetone and ether rather than ether alone, while H. D. Minnig (*Amer. Journ. Sci.*, (4), **39**, 197, 1915) uses a mixture of 1 volume of acetyl chloride and 4 volumes of acetone. R. W. Dodson, G. J. Forney and E. H. Swift (*Journ. Amer. Chem. Soc.*, **58**, 2573, 1936) say that isopropyl ether is much more effective than ethyl ether over a wider range of acid concentrations. From 99·1 to 99·5 per cent. of the total iron is extracted from solutions containing 24 to 31 grms. of hydrochloric acid per 100 c.c. Pentavalent vanadium and hexavalent molybdenum are also extracted.

[2] It must be pointed out that, since the ether initially contains no hydrochloric acid, the amount of hydrochloric acid in the aqueous layer is decreased by each extraction if ordinary ether be used. Hence some use ether slightly acidified with HCl. Ether dissolves 3 per cent. of its volume of water. 10 c.c. of a solution of ether which had been shaken with an equal volume of hydrochloric acid (sp. gr. 1·1033) contained but 0·0019 grm. of HCl. Speller found

solution has much above or below 20 per cent. by weight of hydrochloric acid, the efficiency of the extraction will be impaired. For instance, Speller found that when 0·8 grm. of iron (as ferric chloride) was dissolved in 100 c.c. of hydrochloric acid, of the strength stated, shaken with twice its volume of ether and allowed to stand 30 minutes at 17°–18°, the iron was divided between the ethereal and aqueous layers as indicated in Table LIV. Hence *hydrochloric acid of specific gravity* 1·100–1·115 (22·0 *to* 25·5 *grms. of HCl per* 100 *c.c. of solution*) *is most favourable to the extraction of ferric chloride by ether.*

Effect of Phosphorus. —If phosphorus be present, Wysor [1] has shown that there is an increasing amount of phosphorus lost in the ether layer with an increase in the proportion of iron and phosphorus. But "a fairly constant percentage of the phosphorus present in the solution remains with the iron in the ether separation. The approximate error may therefore be calculated and the proper correction applied." The first line in the following table gives the amount of soluble phosphorus pentoxide in the given sample; and the succeeding lines the weight of phosphorus pentoxide to be added to the weight of the alumina residue found for different amounts of iron:

P_2O_5	.	.	.	.	0·0023	0·0046	0·0092	0·0182	0·0366	grm.
Correction per 1 grm. Fe	.		0·0005	0·0009	0·0016	0·0031	0·0060			,,
Correction per 2 grms. Fe	.		..		0·0015	0·0029	0·0055	0·0108		,,
Correction per 3 grms. Fe	.		..		0·0017	0·0032	0·0064	0·0130		,,

It is assumed that the correction for the intermediate values of phosphorus and iron can be obtained by interpolation.

Extraction of the Iron by Rothe's Pipette. [2] —Rothe's pipette, mounted ready for use, is illustrated in fig. 108. Two mixing cylinders, each of about 200 c.c. capacity, are connected at their lower ends by a 3-way cock. The upper ends of the cylinders are fitted with 2-way stopcocks. The boring of the 3-way cock will be obvious from fig. 109, which shows five different positions, numbered 1 to 5.

The 3-way cock is placed in the position No. 1; the solution under investigation, [3] containing about 23 per cent. of hydrochloric acid (weight/volume) and occupying 50–60 c.c., is poured into the left cylinder by means of the long funnel as shown in the diagram, fig. 108. The beaker and funnel are washed with 23 per cent. hydrochloric acid. Close the left stopcock. Place the funnel in the other cylinder and introduce 100 c.c. of ether. [4] Remove the funnel and close the stopcock. Connect the ether cylinder with the rubber bellows, as shown in the diagram. Open the right stopcock and blow a small quantity of air into the ether cylinder. Turn the 3-way stopcock into the position No. 2, and ether will bubble through the solution in the left cylinder. The

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that when 150 c.c. of anhydrous ether were shaken with 100 c.c. of hydrochloric acid, and allowed to stand 30 minutes at 17°–18°, 100 c.c. of the acid contained:

Ether	.	.	.	140	89	64	30	19	15·5	14·4 c.c.
Sp. gr. acid	.	.	1·177	1·140	1·123	1·103	1·075	1·063	1·055	

The presence of ferric, copper, cobalt and nickel chlorides in the hydrochloric acid slightly modified the solubility of ether in the acid.

[1] R. J. Wysor, *Journ. Ind. Eng. Chem.*, **2**, 45, 1910.

[2] Many other forms of "separating funnels" or "separating pipettes" have been devised, e.g. A. Carnot, *Méthodes d'Analyse des Fontes des Fers et des Aciers*, Paris, 124, 1895.

[3] The solution should be quite clear; if not, filter. Nitric acid and chlorine should be absent. If present, they must be removed by evaporation.

[4] No naked flames must be near while the ether is being used.

ether becomes warm as it mixes with the solution.[1]　When about nine-tenths of the ether has bubbled through the solution, restore the 3-way cock to No. 1
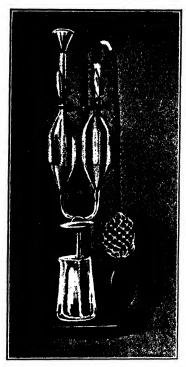
position.　Close the other two cocks.　Cool the cylinder under a stream of cold water and thoroughly agitate the solution under the water tap.　Open the right cock.　Force more air into the right cylinder, and turn the 3-way cock into position No. 2.　The remaining ether passes into the left cylinder.[2] Turn the 3-way stopcock into position No. 1. Close the two remaining cocks and shake the apparatus vigorously.　Let the apparatus remain at rest two or three minutes.　The liquid in the left cylinder separates into two layers.　Open the two 2-way stopcocks, and turn the 3-way cock into position No. 2. When the lower aqueous layer has passed into the right cylinder,[3] so that but a little of the aqueous layer remains in the capillary tube on the left, turn the 3-way cock into position No. 1.　Close the 2-way cocks.　Shake the apparatus, whereby any drops of aqueous liquid adhering to the walls of the left cylinder collect on the bottom.　The ethereal layer will be clear in 5–10 minutes.　Then blow the remaining aqueous liquid into the right cylinder until a little of the ethereal layer appears in the capillary at the bottom of the right cylinder.　Place a beaker below the 3-way stopcock, and turn this cock into the position No. 3.　Open the left 2-way cock, and the ethereal solution containing the ferric chloride flows into the beaker.[4]　Turn the 3-way cock into the position No. 1.　Pour a little ether into the left cylinder.　Close the

FIG. 109.—Bore of 3-Way Stopcock in Rothe's Pipette.

stopcocks; shake; and if any aqueous solution separates, blow it into the right cylinder and run off the excess ether by turning the 3-way cock into the position No. 3 as before.　Turn the 3-way cock into position No. 1. Pour about 50 c.c. of ether into the left cylinder and repeat the preceding

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[1] Some ferric chloride is reduced to ferrous chloride.　But this does not matter.

[2] This procedure prevents error arising from the non-extraction of the liquid in the capillary tubes connecting the two cylinders.

[3] Assisted, if necessary, by connecting the blower with the left cylinder.

[4] If much copper and cobalt be present, appreciable quantities of copper and cobalt chloride will be dissolved by the ether.　In that case, add 10 c.c. of hydrochloric acid (sp. gr. 1·104) to the ethereal solution, shake and draw off the aqueous layer containing the copper and cobalt into a second beaker.

operations, simply reversing the cylinders.[1] This leaves the aqueous solution in the left cylinder. Repeat the operation a third time with another 50 c.c. of ether. This leaves the aqueous solution in the right cylinder.

Treatment of Ethereal Layer.—The three ether extractions will have removed practically all the iron from the aqueous layer. The ethereal solution is transferred to a porcelain basin and evaporated on an electrically-heated water bath at 50°–60°, in order to drive off the ether. The dry residue may then be dissolved in hydrochloric acid and the iron determined in the usual way (page 180).

Treatment of Aqueous Layer.—The aqueous solution, freed from iron, is also run off into another porcelain dish. The funnels are washed with 20 per cent. hydrochloric acid and the solution is evaporated to dryness to remove the ether. It is then ready for any other separations which may be required.

Extraction of the Iron by Soxhlet's Extractor.—Instead of "shaking out" with ether by means of a separating funnel, it may be more convenient to extract the iron from the solution by a modification of Soxhlet's extractor,[2] say Taylor's extractor, illustrated in fig. 110. The solution—25 30 c.c.—is placed in the receptacle *A*; ether is placed in the flask *B*. The latter is heated by a water bath, or an electric lamp. The ether boils, the vapour is condensed in *C*. The condensed liquid runs into *A*, bubbles through the solution and is finally syphoned into the flask *B*. This circulation of the ether will extract all the iron from the solution in a short time. At the end of, say, an hour, when the solution has cooled, the apparatus is disconnected. The ethereal solution of iron in the flask *B*, and the extracted solution in the receptacle *A*, are treated as described above.
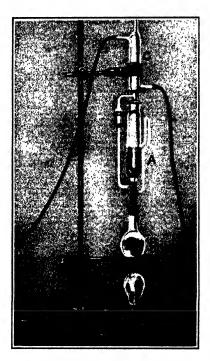
FIG. 110.—Extraction of Liquids with Ether.

§ 250. The Analysis of Iron Oxides, Red Earths and Iron Ores.

The iron in iron ores, iron oxides and red marls can sometimes be extracted by boiling the powdered sample with concentrated hydrochloric acid—with or without a little nitric acid. Nitric acid should always be added if sulphides be present, in order to oxidise the sulphides to sulphates.[3] The silicate ores

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[1] Note the positions of the 3-way cock Nos. 4, 2, 5 for working the right cylinder, compared with Nos. 1, 2, 3 while working the left cylinder.

[2] H. P. Smith, *Chem. News*, **83**, 152, 1901; H. Göckel, *Zeit. angew. Chem.*, **10**, 683, 1897; I. Greenwald, *Journ. Ind. Eng. Chem.*, **7**, 621, 1915.

[3] Otherwise, the results of, say, the dichromate titration will be high. W. F. K. Stock and W. E. Jack, *Chem. News*, **30**, 221, 1874. A. Esilman (*Chem. News*, **30**, 243, 1874) recommends filtering off the insoluble residue before titrating for the iron, in order to eliminate as far as possible the secondary effects of carbonaceous matter, pyrites, etc.

are sometimes more easily decomposed by digestion in acids if they be first calcined at a low temperature [1]; and even if the ore dissolves readily in acids, the silica obtained in the subsequent evaporation (page 147) is cleaner and purer than if the uncalcined ore had been digested directly in acids.[2]

If the sample be not decomposed by digestion in acids, the sodium peroxide fusion may be used, as described on pages 264 and 529. If iron alone is to be determined, the peroxide fusion is usually quite satisfactory for red clays and calcined iron oxides; but several alternative methods have been suggested.[3] The iron, when dissolved, is reduced and determined by titration with permanganate or dichromate.

For a complete analysis, the sodium carbonate fusion (page 144) may be used.[4] A little sodium nitrite (1 to 1·5 grms.) [5] should be added in order to oxidise the sulphides to sulphates. Care must be taken to heat the mixture slowly or loss by spurting may occur. The hygroscopic moisture, combined water, silica,[6] elements precipitated by hydrogen sulphide in acid solution, alumina, iron oxide, phosphoric and titanic oxides are determined as indicated on page 198. The sulphur can be determined in an aliquot portion of the filtrate from the silica; chromium can be determined as indicated on page 521. The filtrate from the basic acetate separation can be used for the determination of manganese, zinc, nickel, cobalt, lime and magnesia. The zinc is first precipitated as sulphide by hydrogen sulphide in dilute (formic or hydrochloric)

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[1] E. Ladd (*Min. Eng. World*, 36, 1350, 1912) proposes to avoid the fusion in the analysis of china clays by utilising this principle, but the method cannot be recommended. W. H. Worthington (*Min. Science*, 63, 521, 1911) recommends opening the sample of ore (in the absence of lime and baryta) with potassium bisulphate, because the silica can be filtered immediately the cold cake has been dissolved up in dilute acid. Fusion, filtration and washing of the silica occupy about 30 minutes.

[2] Though iron oxides resist attack by the acids better after calcination, this is not necessarily the case with silicates calcined at, say, dull redness. H. Rocholl, *Zeit. anal. Chem.*, 20, 289, 1881; G. W. Dean, *Journ. Amer. Chem. Soc.*, 28, 882, 1906; H. E. Ashley, *Chem. News*, 90, 274, 1904.

[3] R. W. E. MacIvor (*Chem. News*, 29, 246, 1874; B. Krieger, *Chem. Ztg.*, 35, 1054, 1911) states that the iron in hæmatites readily dissolves as ferrous iron when the finely powdered material is digested in a long-necked flask with sulphuric acid and metallic zinc until all action has ceased. The iron is in the ferrous condition ready for titration with potassium permanganate. H. Bornträger (*Zeit. anal. Chem.*, 35, 170, 1896; 38, 774, 1899) says that ignited ferric oxide dissolves at once in HCl provided a little iron-free manganese dioxide be added. This is probably due to the formation of chlorine. A. Classen (*Zeit. anal. Chem.*, 17, 182, 1878) says that ignited ferric oxide dissolves at once in concentrated hydrochloric acid if the powdered material be previously boiled to a flocculent condition with caustic potash solution. The alkaline liquid is decanted off and the acid added. T. M. Brown (*Iron*, 361, 1878; *Dingler's Journ.*, 228, 378, 1878; E. Donath and R. Jeller, *Zeit. anal. Chem.*, 25, 361, 1886) ignites the powdered material intimately mixed with from half to its own volume of powdered zinc. The mixture is ignited in a porcelain crucible for 5–8 minutes. The mass is transferred from the crucible to a flask and dissolved in dilute sulphuric acid (1 : 2). Portions adhering to the crucible can be removed by washing with dilute acid. The zinc must be free from iron. The ferric oxide is reduced to metal. Chromium oxide and alumina are not reduced to metals by the ignition with zinc powder. H. von Jüptner (*Oester. Zeit. Berg. Hütt.*, 42, 469, 1894) recommends magnesium powder in place of zinc. E. Hart (*Chem. News*, 34, 65, 1876; J. S. Maclaurin and W. Donovan, *Journ. Soc. Chem. Ind.*, 28, 827, 1909) reduces the ore in a stream of hydrogen gas for 10–30 minutes (page 267). The sample is then usually easily decomposed by hot dilute acid. F. Michel, *Chem. Ztg.*, 36, 345, 1912; J. J. Morgan, *Journ. Soc. Chem. Ind.*, 13, 1024, 1894.

[4] For the error produced by solution of platinum when iron ores are fused in platinum crucibles, see footnote 6, p. 500.

[5] Potassium nitrate is generally recommended for this purpose. The nitrite neither froths nor attacks the crucible so much as the nitrate.

[6] G. W. Dean, *Journ. Amer. Chem. Soc.*, 28, 882, 1906; 29, 1208, 1907; T. G. Timby *ib.*, 30, 614, 1908; H. E. Ashley, *Chem. News*, 90, 274, 1904.

acid solution (page 385). The mixed sulphides of manganese,[1] nickel and cobalt are then precipitated by hydrogen sulphide in ammoniacal solution as indicated on page 415. The magnesia and lime are determined in the filtrate. The residual mixed sulphides are taken up with aqua regia (page 416), the solution neutralised with sodium carbonate, acidified with acetic acid and treated with hydrogen sulphide, whereby nickel and cobalt sulphides are precipitated, as described on page 416.

§ 251. The Determination of Ferrous Oxide.

Iron existing in the ferrous condition is rarely reported in clay analyses, and when the relative proportions of ferrous and ferric oxides are indicated the results are usually of little or no value. One reason is that no satisfactory general method is known for the determination of the ferrous iron in clays containing organic matter.[2] A number of different methods have been suggested for decomposing silicates without interfering with the state of oxidation of the iron. For example:

(1) Fusion with sodium carbonate. The objection to this process is the risk of absorbing air during the fusion and the consequent oxidation of the manganese. The manganates, later on, oxidise the ferrous salts, leading to low results when the solution of the fused mass is titrated with permanganate.[3]

(2) Fusion with borax—Hermann's process. Here high results are obtained owing to the reduction of ferric salts during the fusion.[4]

(3) Digestion in a sealed glass tube with sulphuric acid, or a mixture of hydrofluoric [5] and sulphuric acids, at 150°–200°. This method furnishes very fair results in the absence of sulphides.[6]

(4) Digestion in a platinum crucible with a mixture of hydrofluoric and sulphuric acids, in an atmosphere of carbon dioxide.[7]

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[1] V. Macri, *Monit. Scient.*, (4), **20**, 18, 1906; A. Kaysser, *Chem. Ztg.*, **35**, 94, 1911 (bog iron ores); F. Michel, *Chem. Ztg.*, **36**, 345, 1912.

[2] N. F. Solov'eva (*Proc. Leningrad Dept. Inst. Fert.*, **17**, 21, 1933) gives a method for the determination of ferrous iron in the presence of organic matter.

[3] W. Early, *Chem. News*, **30**, 169, 1874.

[4] R. Hermann, *Journ. prakt. Chem.*, (1), **15**, 105, 1838; W. Suida, *Tschermak's Mitt.*, (1), **5**, 176, 1876; C. Bodewig, *Pogg. Ann.*, **158**, 222, 1876; C. Rammelsberg, *Zeit. deut. Geol. Ges.*, **24**, 69, 1872; H. Rose, *Handbuch der analytischen Chemie*, Braunschweig, **2**, 699, 1871.

[5] Presumably the hydrofluoric acid is not exhausted by attacking the glass before it has had time to react with the substance under investigation. According to W. F. Hillebrand (*Bull. U.S. Geol. Sur.*, **700**, 193, 1919), the addition of hydrofluoric acid is "of very doubtful utility."

[6] A. Mitscherlich, *Journ. prakt. Chem.*, (1), **81**, 116, 1860; (1), **83**, 445, 1861; *Zeit. anal. Chem.*, **1**, 56, 1862; C. Doelter, *ib.*, **18**, 50, 1879; *Tschermak's Mitt.*, (1), **7**, 281, 1877; (2), **3**, 100, 1880; A. Remelé, *Notizblatt*, **3**, 160, 1867; **4**, 173, 1868. W. Michaelis (*ib.*, **5**, 204, 1869) says all the clay is not decomposed. For hydrochloric acid in sealed tubes—A. H. Allen, *Chem. News*, **22**, 57, 1870; S. Piña de Rubies, *Anales Fis. Quim.*, **10**, 78, 1912; *Chem. Ztg.*, **36**, 570, 1912. For operating with sealed tubes, consult page 551.

[7] G. Werther, *Journ. prakt. Chem.*, (1), **91**, 321, 1864; J. P. Cooke, *Amer. J. Science*, (2), **44**, 347, 1867; J. H. Pratt, *ib.*, (3), **48**, 149, 1894; F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, **2**, 415, 1911; F. Mohr, *Zeit. anal. Chem.*, **7**, 450, 1868; A. R. Leeds, *ib.*, **16**, 323, 1877; C. Doelter, *ib.*, **18**, 50, 1879; O. Hackl, *ib.*, **67**, 197, 1925; C. E. Avery, *Chem. News*, **19**, 270, 1869; O. L. Barnebey, *Journ. Amer. Chem. Soc.*, **37**, 1481, 1915; L. A. Sarver, *ib.*, **49**, 1472, 1927; C. J. Schollenberger, *ib.*, **53**, 88, 1931; W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **700**, 203, 1919; E. Salvatore and A. Squco, *Zeit. Krist.*, **66**, 162, 1927; H. Heinrichs, *Glastech. Ber.*, **5**, 154, 1927; A. E. J. Vickers, *Trans. Cer. Soc.*, **27**, 156, 1928; M. S. Kovtun, *Zavodskaya Lab.*, **5**, 1042, 1936; N. E. Densem, *Journ. Soc. Glass Tech.*, **20**, 309, 1936; C. A. Wilbur and W. Whittlesey (*Chem. News*, **22**, 2, 1870) use a mixture of calcium fluoride and hydrochloric acid; and A. H. Chester and F. I. Cairns (*Amer. J.*

The silicate, when decomposed by one of the methods—(4) for preference—indicated above, is titrated with a standard solution of potassium permanganate for the ferrous iron.[1]

Dissolution of the Ferrous Iron. From 0·3 to 1 grm. of the sample, powdered as coarsely as will permit of its decomposition by the acids in a reasonable time,[2] is placed in a platinum crucible or dish—approximately 40–50 c.c.—and stirred up with 15 c.c. of dilute sulphuric acid (1 : 3).[3] The stirring must be thorough, since the powder may "cake" at the bottom of the dish and escape attack by the acids later on. Place the crucible A on a support, fig. 111, in Treadwell's decomposition vessel,[4] which consists of a leaden box B supported in a paraffin wax [5] bath C. The leaden cover has two holes D and E. A rapid stream of carbon dioxide gas [6] is passed through D for about 5 minutes. The lead cover is removed and about 10 c.c. of concentrated hydrofluoric

FIG. 111.—Treadwell's Apparatus (Section).

Science, (3) 34, 113, 1883) use a mixture of ammonium fluoride and sulphuric acid. B. A. Soule (*Journ. Amer. Chem. Soc.*, 50, 1691, 1928; 51, 2117, 1929) decomposes the material in a hard glass flask and titrates the ferrous iron electrometrically with ceric sulphate. For a discussion of methods, see V. Smirnov and N. Aidinyan, *Compt. rend. Acad. Sci. (U.S.S.R.)*, 14, 353, 1937, and O. Hackl (*Mikrochem.*, 21, 224, 1937) for the detection of FeO and Fe₂O₃ in silicates.

[1] J. M. Eder (*Monats.*, 1, 137, 140, 1880) suggests the following gravimetric process for the determination of ferrous oxide in the presence of organic matter and ferric oxide. The solution must not be too strongly acid:—Add an excess of neutral potassium oxalate and silver nitrate. In a few minutes add sufficient tartaric acid to prevent the precipitation of ferric hydroxide on addition of ammonia. Add an excess of ammonia. The addition of some ammonium chloride here favours the filtration and washing of the precipitate. The precipitated silver may be dissolved in nitric acid, precipitated and weighed as silver chloride. From this, the ferrous oxide can be determined by computation from the equation: $2FeO + Ag_2O = Fe_2O_3 + 2Ag$. Hence 1 grm. of silver represents 0·6658 grm. FeO; or 1 grm. of silver chloride represents 0·5012 grm. FeO. For a method for the determination of ferrous and ferric oxides and metallic iron in the presence of one another, see F. Kaufmann, *Chem. Ztg.*, 57, 122, 1933; T. Tazawa, *Seitetsu Kenkyu*, No. 134, 1933. For the separation of ferrous and ferric oxides in silicates by digesting the powdered mineral in a sealed tube with a mixture of potassium iodide and hydrochloric acid at 120°, see H. Schnerr, *Beiträge zur chemischen Kenntnis des Granitgruppe*, München, 1894; *Zeit. anorg. Chem.*, 7, 369, 1894.

[2] Some silicates—particularly those poor in silica and rich in magnesia—are liable to "cake" on the bottom of the crucible and escape attack by the acid. M. Dittrich (*Ber.*, 44, 990, 1911) recommends that the powdered mineral be intimately mixed with coarsely ground quartz, which resists attack by the hydrofluoric acid long enough for the mixed acids to attack the mineral. The quartz also exposes a larger surface of the mineral to the attack. N. E. Densem (*l.c.*) boils the mixture of acids in the crucible in an atmosphere of carbon dioxide for 15 minutes to expel dissolved oxygen before adding the powdered sample.

[3] If carbonates be present the mixture may effervesce. Hence the acid must be added slowly to the dish, covered with a watch-glass to prevent loss by spurting. The cover must be afterwards rinsed into the dish. There is little danger of oxidation of the ferrous iron at this stage.

[4] F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, 2, 416, 1911. For a convenient modification, see N. E. Densem, *Journ. Soc. Glass Tech.* 20, 309, 1936.

[5] Instead of paraffin wax, L. W. Bosart (*Journ. Amer. Chem. Soc.*, 31, 724, 1909; *Chem. News*, 100, 238, 1909) recommends a mixture of 10 parts refined cotton seed oil and 1 part of beeswax. It fumes but little below 250°, and its flash-point in an open cup is above 300°; hard paraffin wax under the same conditions flashed at 215°. Like paraffin wax, the mixture solidifies on cooling, but it melts more quickly. Special oils, with a flash-point over 300°, are now sold for charging oil baths.

[6] Purified as indicated on page 174, footnote 7.

acid [1] (40 per cent.) is added to the crucible. The crucible is placed directly under the opening E. This permits its contents to be stirred with a stout platinum wire. The bath is now heated to about 100° and maintained at that temperature for about an hour. The aperture T allows a thermometer to be placed in the paraffin bath C. Some of the excess of hydrofluoric acid may be driven off by raising the temperature to 120° for another hour. It is important not to work too long at the higher temperature lest oxidation result. There should now be no grit representing undecomposed mineral in the crucible. The use of silicic acid later on renders a prolonged heating to drive off hydrofluoric acid unnecessary. Keep the stream of carbon dioxide flowing through the apparatus all the time. Let the system cool, while still maintaining the current of gas.

An alternative and simpler method of decomposing the mineral—not quite so effective—is as follows:—

Fit a 50 c.c. platinum crucible tightly into a hole in the centre of a piece of asbestos millboard so that the crucible passes about half-way through, and the joint between the crucible and asbestos is nearly air-tight. Moisten half a gram of the coarsely powdered sample in the crucible with water. Put in a couple of coils of platinum wire to prevent bumping. Add a cold mixture of 10 c.c. of hydrofluoric acid and 15 c.c. of dilute sulphuric acid (1 : 3). Cover the crucible with a tight-fitting lid.[2] Connect the stem of a 15 cm. funnel [3] with a carbon dioxide generator. The funnel is placed over the crucible and it should fit close to the asbestos millboard. When the air has been expelled by the carbon dioxide, a Bunsen burner is placed below the crucible (fig. 112) so that the tip of the flame is about 3 inches below the bottom of the crucible, and the flame is raised or lowered until the contents of the crucible boil gently. The motion prevents the particles of silicate from caking on the bottom. In 5 or 10 minutes the mineral will be decomposed. The burner is removed. When the steam in the crucible has condensed, the crucible is lifted with a pair of tongs,[4] without removing the lid, and plunged into a 600 c.c. beaker containing 400 c.c. of cold, recently boiled distilled water, 20–25 grms. of potassium sulphate and 20 grms. of pure silicic acid.[5] The lid of the crucible is removed and the contents are ready for titration.[6]

Titration for the Ferrous Oxide.—Stir the mixture thoroughly and titrate as rapidly as possible with standard permanganate (page 180). The first permanent pink blush is the end-point. This fades in a short time. It is well to confirm the method by a blank test, or with ferrous sulphate solution which has been standardised with hydrofluoric acid. To obviate the fading

[1] Hydrofluoric acid may contain reducing agents, *e.g.* arsenious acid, hydrogen sulphide— C. Jehn, *Zeit. anal. Chem.*, **13**, 176, 1874; *Archiv Pharm.*, (3), **1**, 481, 1873. If the acid be made in leaden vessels it frequently contains sulphurous acid. If present, this must be destroyed by the addition of potassium permanganate until the colour just ceases to be discharged—W. Hampe, *Chem. Ztg.*, **15**, 1777, 1891. See pages 149 and 219. V. Smirnov and N. Aidinyan (*l.c.*) cover the reaction mixture with a layer of toluene or with a solution of paraffin wax in toluene to prevent bumping on heating.

[2] L. A. Sarver (*Journ. Amer. Chem. Soc.*, **49**, 1472, 1927) uses a transparent bakelite cover, fitted with an entrance tube and funnel, also of bakelite. See also C. J. Schollenberger, *Journ. Amer. Chem. Soc.*, **53**, 88, 1931.

[3] Coated inside with paraffin wax.

[4] A loop of platinum wire may be fixed round the crucible before it is placed on the asbestos millboard, for convenience in lifting and transferring the hot crucible to the beaker of water.

[5] Or enough to neutralise all the hydrofluoric acid which is present.

[6] A reddish-brown sediment which dissolves when stirred up with water is not to be mistaken for undecomposed mineral.

end-point, the addition of boric acid, instead of silica and potassium sulphate, has been recommended, as the hydrofluoric acid is thereby inactivated through the formation of hydrofluoboric acid, HBF_4.[1] Schollenberger [2] says that if the ferrous iron be titrated with standard dichromate, using diphenylamine as indicator, the presence of free hydrofluoric acid is actually an advantage, since
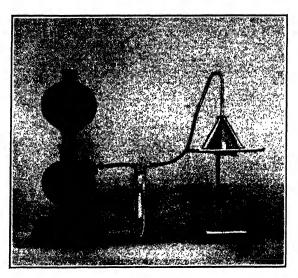
FIG. 112.—Opening Silicates for the Determination of Ferrous Iron.

it intensifies both the colour and sharpness of the end-point—hence he recommends the omission of boric acid or similar reagents. One grm. of $KMnO_4$ represents 2·273 grms. of FeO, which, in turn, is equivalent to 2·526 grms. of Fe_2O_3. Hence calculate the ferrous oxide to ferric oxide and subtract the result from the total amount of ferric oxide determined in the sodium carbonate fusion as indicated on page 180.

EXAMPLE.—The sodium carbonate fusion, etc. (page 164), furnished 3·65 per cent. of Fe_2O_3. In the above determination, 1 grm. of the sample required 6·2 c.c. of permanganate containing 0·00098 grm. $KMnO_4$ per c.c. That is, 0·006076 grm. $KMnO_4$, i.e. 0·006076 × 2·273 grm. FeO. Hence the substance has 0·0138 grm. of FeO. But 0·0138 grm. FeO corresponds with 0·006076 × 2·526 = 0·0153 grm. Fe_2O_3, that is, 1·53 per cent. Fe_2O_3. Hence the sample has 3·65 less 1·53 = 2·12 per cent. of ferric oxide —Fe_2O_3.

It is probable that the results for ferrous oxide are usually a little too low.

§ 252. Disturbing Factors in the Determination of Ferrous Oxide.

This subject has been carefully studied by Hillebrand and Stokes, and after a comparison of the different methods in use for the determination of ferrous oxide in silicates insoluble in the mineral acids, it has been stated by Hillebrand that, "despite the utmost care in practical manipulation, the exact

[1] O. L. Barnebey, *Journ. Amer. Chem. Soc.*, 37, 1481, 1829, 1915; L. A. Sarver, *l.c.*
[2] C. J. Schollenberger, *l.c.*; M. S. Kovtun, *Zavodskaya Lab.*, 5, 1042, 1936.

determination of ferrous iron in rocks is fraught with extraordinary difficulties and uncertainties. Only in the absence of decomposable sulphides and carbonaceous matter, and when the amount and condition of the vanadium are known and relatively coarse powders can be used, is it permissible to regard the result as fairly above suspicion."

1. *The Influence of Fine Grinding.*—The unavoidable oxidation of ferrous compounds during grinding was discussed on page 107. "Nearly all mineral analyses which have been made in the past are affected by more or less serious errors in respect not only to the oxides of iron but also to water, the error being greater the further the comminution of the sample was carried " (Hillebrand).

2. *The Influence of Sulphides.*— When sulphides decomposable by the acids are present, some hydrogen sulphide and possibly also some sulphur dioxide are formed.[1] These gases will reduce some of the ferric oxide to ferrous oxide, and consequently the decomposed silicate will contain more ferrous iron than the undecomposed silicate. This is more particularly noticed when the decomposition of the silicate is effected in sealed tubes. The difference between the values obtained by sealed tube and open decompositions is not very marked when but small quantities—2 per cent.—of ferrous iron are present, but the error may amount to nearly 2 per cent. when about 10 per cent. of ferrous iron is present. 0·01 per cent. of sulphur may cause the ferrous oxide to appear 0·135 per cent. too high, on the assumption that the sulphide sulphur is oxidised to sulphur trioxide. If the sulphide sulphur is liberated as hydrogen sulphide and this is subsequently oxidised to sulphuric acid, the error will amount to 0·18 per cent. for every 0·01 per cent. of sulphur so oxidised. The oxidation of the sulphides to sulphates and the consequent reduction of the ferric oxide, are greatly accelerated by the presence of ferric salts. The acid mixture will scarcely attack pyrite, but in the presence of ferric salts the action is relatively quick. Nevertheless, when but small quantities of pyrite are present, its influence on the determination of ferrous iron by the process outlined on page 512 is negligible. "At the same time it is to be borne in mind that with increased content in ferric iron an increased amount of pyrite will be attacked, and that the extent of this attack is influenced by the degree of fineness of the pyrite powder, which itself undergoes oxidation during grinding." [2] If an acid-soluble sulphide, such as pyrrhotite, be present the bulk of the iron in it may also appear in the final titration as ferrous iron.

3. *The Influence of Organic Matter.*—Carbonaceous matter will reduce the sulphuric acid in the sealed tube method; and, in general, organic matter will reduce the ferric oxide and render the determination of the ferrous iron in a mixture nugatory.[3]

4. *The Influence of Vanadium.*—If appreciable quantities of vanadium be

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[1] E. A. Wülfing, *Ber.*, 32, 2217, 1899; J. H. L. Vogt, *Zeit. prakt. Geol.*, 7, 250, 1899; L. L. de Koninck, *Ann. Soc. Géol. Belgique*, 10, 101, 1883; *Zeit. anorg. Chem.*, 26, 123, 1901; W. F. Hillebrand and H. N. Stokes, *Journ. Amer. Chem. Soc.*, 22, 625, 1900 ; H. N. Stokes, *Amer. J. Science*, (4), 12, 414, 1901. T. Scheerer (*Pogg. Ann.*, 124, 98, 1850) compared the results obtained by the different methods. See also A. Leonhard, *Ueber die Bestimmung des Eisenoxyduls in Gesteinen*, Heidelberg, 1912.

[2] W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, 700, 202, 1919. If the sulphides have been determined, a correction can sometimes be made for them.

[3] J. T. Hewitt and G. R. Mann (*Analyst*, 37, 179, 1912) titrate solutions of ferric iron in presence of organic matter with standard thiosulphate solution, using ammonium thiocyanate as indicator and a small quantity of copper sulphate as catalyst. The titration is continued until the red colour of the ferric thiocyanate disappears. The end-point is not sharp, and better results are obtained by adding a slight excess of the standard thiosulphate, and titrating back the excess with an iodine solution, using starch as indicator.

present as, say, V_2O_3,[1] a correction must be made for the permanganate used in converting $V_2O_3 \rightarrow V_2O_5$ during the titration (page 181). Every gram of V_2O_3 found in the sample will be equivalent to 1·9171 grms. of FeO in the consumption of permanganate. If the vanadium occurs in the form of V_2O_5, no correction will be required.

EXAMPLE.—If a silicate contains 0·11 per cent. of V_2O_3, and the FeO, calculated from the permanganate titration, is 2·11 per cent., it follows that $0·11 \times 1·9171 = 0·21$ per cent. is not FeO. The FeO corrected for the vanadium will then be 2·11 less $0·21 = 1·90$ per cent. FeO.

5. *Influence of Hydrofluoric Acid on the Permanganate Titration.*—A solution of ferrous sulphate in fairly concentrated sulphuric acid oxidises somewhat slowly; but if a little hydrofluoric acid be added to the solution, the rate of oxidation is considerably increased. Hence it is very important to expose the solutions containing ferrous iron as little as possible to the air before titration.

According to Pugh [2] fluorides have no influence in alkaline solution, but in acid solution the reduction of the permanganate tends to be arrested at the stage of trivalent manganese, especially when weak reducing agents are used. High concentrations of hydrochloric acid offset this tendency.

This discussion all shows that the presence of the hydrofluoric acid interferes with the accuracy of the permanganate titration. In the presence of hydrofluoric acid, the permanganate is decolorised very quickly, so that the permanent pink blush normally obtained with permanganate titrations is very fugitive in the presence of hydrofluoric acid. It is therefore difficult to get a distinct end-point. At the best, the pink blush lasts but a few seconds, and it is even more fugitive with increasing amounts of ferrous oxide and of hydrofluoric acid. If the solution be boiled some time with the idea of driving off part of the hydrofluoric acid, part of the ferrous iron may be transformed to ferric iron by the oxidising action of the sulphuric acid as it becomes more and more concentrated. Gage [3] states that hydrofluoric acid does not interfere with the titration in the presence of calcium phosphate, but, according to Leonhard, the action is then so slow that the end-point is uncertain. Dittrich and Leonhard recommend the addition of 1 to 2 grms. of potassium or sodium sulphate (not ammonium sulphate) to the mixture to facilitate the recognition of the end-point of the permanganate titration.[4] That being the case, it is advisable to spend less time in driving off the excess of hydrofluoric acid, and avoid getting low results arising from the oxidation of ferrous iron during the concentration of the solution. Fromme also avoids the danger of oxidation during the removal of hydrofluoric acid by neutralising the hydrofluoric acid with pure silica. The resulting hydrofluosilicic acid enables the titration to be conducted more accurately than in the presence of hydrofluoric acid. Alternative methods have been discussed on page 514.

[1] C. Czudnowicz, *Pogg. Ann.*, **120**, 20, 1863; O. Lindemann, *Zeit. anal. Chem.*, **18**, 99, 1879; W. F. Hillebrand and F. L. Ransome, *Amer. J. Science*, (4), **10**, 120, 1900.

[2] W. Pugh, *Trans. Roy. Soc. S. Africa*, **22**, 71, 1934.

[3] H. Fromme, *Tschermak's Mitt.*, **28**, 329, 1909; R. B. Gage, *Journ. Amer. Chem. Soc.*, **31**, 381, 1909; G. J. Hough, *ib.*, **32**, 545, 1910. M. Dittrich and A. Leonhard, *Ber. Vers. Oberrhein. geol. Ver.*, **2**, 92, 1910; *Zeit. anorg. Chem.*, **74**, 21, 1912; O. Follenius, *Zeit. anal. Chem.*, **11**, 117, 1872; E. Rupp, *Ber.*, **38**, 164, 1905; A. Leonhard, *Ueber die Bestimmung des Eisenoxyduls in Gesteinen*, Heidelberg, 1912. S. Shinkai and K. Takahashi (*Journ. Soc. Chem. Ind. Japan*, **38**, Suppl., 133, 266, 1935) say that inaccuracies in the determination of ferrous oxide in glass by permanganate are due more to the presence of arsenic than to the hydrofluoric acid.

[4] E. Deussen (*Zeit. anorg. Chem.*, **44**, 425, 1905; *Monats.*, **28**, 163, 1907) recommends manganese sulphate; but this is apparently a mistake—W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **700**, 198, 1919.

6. *Influence of Manganous Salts.*—The manganous salt formed by the reaction between the permanganate and the ferrous iron is itself readily oxidised by permanganate in the presence of hydrofluoric acid, so that a sharp end reaction is difficult to obtain if much hydrofluoric acid be present, or if much manganous sulphate be present. The latter will occur when much ferrous iron is under investigation, so that the pink tint of the permanganate persists longer when but little ferrous iron is in question than with larger amounts. The more hydrofluoric acid used, the greater the apparent amount of ferrous iron found.[1]

7. *Influence of Titanium.*—According to Dittrich and Leonhard, titanium sesquioxide, Ti_2O_3, in the presence of ferric salts produces disturbing effects on the end-point in the permanganate titration, and titanium is nearly always present in the analysis of silicate rocks. These effects can be obviated by pouring the contents of the crucible containing the hydrofluoric acid, etc., into a 600 c.c. beaker containing 100 c.c. of water mixed with about 10 grms. of precipitated silica, and 20 25 grms. of potassium sulphate. The mixture is quickly titrated with $0·05N\text{-}KMnO_4$. Hillebrand points out[2] that trivalent titanium and iron cannot co-exist in acid solution since the former is oxidised by ferric iron to the tetravalent state. Thus the only influence trivalent titanium, even if present, would have on the determination would be to increase the apparent amount of ferrous oxide through reduction of the ferric salts present.

[1] F. J. Metzger and L. E. Marrs, *Journ. Ind. Eng. Chem.*, **3**, 333, 1911.
[2] W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **700**, 198, 1919.

THE DETERMINATION OF CHROMIUM, VANADIUM AND URANIUM.

§ 253. The Errors due to the Presence of Chromium, Vanadium and Uranium in Clays.

VANADIUM is a fairly common constituent of fireclays.[1] If chromium, vanadium and uranium be present in a silicate, they will be precipitated with the aluminium, iron and titanium.[2] Consequently, these elements will be found in the products of the pyrosulphate fusion and, if ignored, they may introduce two errors in the analysis:

1. *The iron determination will be too high.* Vanadic oxide—V_2O_5—is reduced by hydrogen sulphide and ammonium bisulphite to V_2O_4, and similarly by silver [3] and hydriodic acid [4]; by magnesium in sulphuric acid solution to V_2O_3; and by metallic zinc, more or less completely to V_2O_2.[5] The colour of the solution undergoing reduction passes from yellowish (V_2O_5) to blue (V_2O_4), to green (V_2O_3), to lavender (V_2O_2). The reduced oxides—V_2O_4, V_2O_3 and V_2O_2—are converted to V_2O_5 by titration with permanganate. Consequently, the action of, say, one molecule of V_2O_3 on the potassium permanganate will be equivalent to the effect of two molecules of reduced ferric oxide; and the action of a molecule of V_2O_4, the same as one molecule of reduced ferric oxide. Hence, with the ammonium bisulphite reduction, every gram of vanadium

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[1] A. Terreil, *Compt. rend.*, **51**, 94, 1860; A. Fioletov, *Keram. Rundsch.*, **35**, 270, 1927.

[2] Note, if certain members of the hydrogen sulphide group be removed before the ammonia precipitation is made, some uranium may be precipitated in that group. The addition of an *excess* of hydrogen peroxide before ammonia will prevent vanadium precipitating with the aluminium group—W. W. Clark, *Met. Chem. Eng.*, **11**, 91, 1913. The whole of the vanadium is not necessarily precipitated in all circumstances with the aluminium group, but "for all practical purposes it is probably safe to assume that the small amounts of vanadium met with in rocks are wholly in the alumina precipitate"—W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **700**, 122, 1919.

[3] G. Edgar, *Journ. Amer. Chem. Soc.*, **38**, 1297, 1916.

[4] P. E. Browning, *Amer. Journ. Science*, (4), **2**, 185, 1896; C. C. Perkins, *ib.*, (4), **29**, 540, 1910; P. Hett and A. Gilbert, *Zeit. öffentlich Chem.*, **12**, 265, 1906; T. Warynski and B. Mdivani, *Mon. Sci.*, **22**, 527, 1908; T. F. Rutter, *Zeit. anorg. Chem.*, **52**, 368, 1907; H. Ditz and F. Bardach (*Zeit. anorg. Chem.*, **93**, 97, 1915) say that reduction proceeds to the tervalent state, but this is possibly an error.

[5] F. A. Gooch and R. D. Gilbert, *Zeit. anorg. Chem.*, **35**, 420, 1903; C. Czudnowicz, *Pogg. Ann.*, **120**, 17, 1863. The statement by B. Glasmann (*Ber.*, **38**, 600, 604, 1905) that metallic zinc reduces V_2O_5 to V_2O_2, while metallic magnesium reduces V_2O_5 to V_2O_3, while both agents reduce molybdic acid to molybdenum sesquioxide, was also proposed as a volumetric process, with the permanganate titration, for the simultaneous determination of vanadium and molybdenum. F. A. Gooch and G. Edgar (*Amer. J. Science*, (4), **25**, 233, 1908; *Chem. News*, **98**, 2, 1908), however, have shown that the action of magnesium is somewhat irregular. For a study of the conditions under which the sulphur dioxide reduction will reduce vanadium pentoxide to the tetroxide, and not attack molybdenum trioxide, see G. Edgar, *Amer. J. Science*, (4), **25**, 332, 1908; *Chem. News*, **97**, 245, 1908. A solution containing vanadium dioxide cannot be exposed to the air momentarily without undergoing oxidation.

pentoxide, V_2O_5, corresponds with 0·8778 grm. of ferric oxide—Fe_2O_3—and with the magnesium reduction, to 1·7556 grms. of ferric oxide.[1]

EXAMPLE.—A fireclay containing 0·09 per cent. of vanadium pentoxide showed 2·15 per cent. of ferric oxide by the ammonium bisulphite reduction and permanganate titration. Hence the effect of the reduced vanadic oxide was the same as 0·09 × 0·8778 = 0·08 grm. Fe_2O_3. Hence the clay had 2·15 less 0·08 = 2·07 per cent. of ferric oxide.

Chromic acid and the chromates are reduced by hydrogen sulphide, metallic zinc, magnesium and aluminium in acid solution, by sulphites and by stannous chloride. Uranium salts are also reduced by similar agents. The reduced salts are reoxidised by potassium permanganate. Hence both chromium and uranium salts will introduce errors in the determination of iron by the titration process. If, therefore, appreciable quantities of these elements are present, methods of separation must be used, and an allowance made.

2. *The titanium determination will be too high.* Vanadium compounds give a reddish-brown—"brick-red"—coloration with hydrogen peroxide. This is a more intense coloration than the yellowish-orange tint due to titanium, and, in consequence, vanadium may intensify the effect of titanium in Weller's colorimetric process, and thus lead to high results. An experienced eye can frequently recognise the presence of vanadium from the tint of the solution prepared for the colorimetric determination of titanium.[2]

§ 254. The Detection of Chromium and Vanadium.

Fuse, say, 5 grms. of the finely powdered silicate with 20 grms. of sodium carbonate[3] and 3-4 grms. of sodium nitrite. Extract the cold cake with hot water and add a little alcohol to reduce the sodium manganate. Filter the solution. The filtrate contains some alumina, silica, arsenic, phosphorus, fluorine, chlorine, sulphur, molybdenum, chromium, vanadium and tungsten; the residue may contain titanium, iron, uranium,[4] barium, zirconium and

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[1] Gooch and Newton's plan (page 172) for the oxidation of Ti_2O_3 without the oxidation of ferrous oxide does not work with reduced vanadium salts, since the degree of reoxidation, produced by the bismuth oxide, depends on the experimental conditions—see W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **700**, 122, 1919.

[2] According to H. J. H. Fenton (*Journ. Chem. Soc.*, **93**, 1064, 1908), a cold aqueous solution of dihydroxymaleic acid gives a straw-yellow coloration in the presence of 1 part of titanium (as titanic salt, say $TiCl_4$) in 1,000,000 parts of solution; a lemon-yellow with 1 : 150,000; and an intense orange-red with 1 : 15,000. The coloration is approximately "fifteen to twenty times as delicate as the hydrogen peroxide test," and "it is not given by vanadium." Molybdates and uranyl salts give red or brown colours, which are destroyed by acids—the former by heating, the latter in the cold. Tungstic acid gives a brown coloration which immediately becomes blue. Negative results are obtained with silica, salts of thorium, cerium, zirconium and tin. Ferric salts interfere by destroying the reagent. Ferrous salts do not interfere. Hence the reaction can be used for detecting titanium in presence of vanadium.

[3] H. L. Robinson (*Chem. News*, **70**, 199, 1894) reports the presence of vanadium in commercial sodium hydroxide.

[4] Treat the residue with nitric acid, and test by boiling the solution with an excess of sodium carbonate. It is perhaps advisable to indicate here a few of the *important reactions of uranium salts.* Potassium hydroxide with uranic salts precipitates a yellow potassium diuranate, $K_2U_2O_7$; ammonium hydroxide, a yellow ammonium diuranate, $(NH_4)_2U_2O_7$; sodium carbonate, a yellow uranyl sodium carbonate, $UO_2Na_4(CO_3)_3$. Ammonium sulphide precipitates a brown uranyl sulphide, UO_2S, which is soluble in ammonium carbonate and in dilute acids. Uranyl salts accordingly give no precipitate with ammonium sulphide in the presence of ammonium carbonate. Potassium ferrocyanide gives a brown precipitate of uranyl ferrocyanide, either $UO_2 . K_2Fe(CN)_6$ or $(UO_2)_2Fe(CN)_6$. Sodium phosphate gives a yellowish-white uranyl phosphate, UO_2HPO_4, which passes into ammonium uranyl phosphate in the presence of ammonium salts.

rare earths. Nearly neutralise the filtrate with nitric acid, but keep the sodium carbonate in slight excess. Evaporate the solution to dryness, take up the mass with water and filter. Add mercurous nitrate to the alkaline solution, when mercurous arsenate, chromate, molybdate and tungstate may be precipitated. Boil the solution and filter. Dry and ignite the precipitate in a platinum crucible, fuse with sodium carbonate and extract the fused mass with water.

Chromium.— A yellow solution probably indicates chromium.[1] The tint of the solution deepens on the addition of, say, sulphuric acid. Pour a little of the solution into a test tube, add an excess of hydrogen peroxide and shake up the mixture with 3 c.c. of ether.[2] A blue coloration in the ethereal solution floating on the aqueous solution indicates chromium.[3] See page 541.

Cazeneuve's Test.— Cazeneuve[4] has shown that diphenylcarbazide, $CO(NH.NH.C_6H_5)_2$, is an extremely delicate reagent for chromium as chromate and the test is far more sensitive than that with hydrogen peroxide. The reagent is prepared by dissolving 0·2 grm. of diphenylcarbazide in 10 c.c. of acetic acid and diluting to 100 c.c. The chromate solution is acidified with acetic, hydrochloric or sulphuric acid and a few drops of the solution of the reagent are added. A violet-pink colour develops and the test is said to be sensitive to one part in several millions. Mercury and molybdenum interfere, hence they must first be removed, if present, by hydrogen sulphide as in the vanadium test (*v. infra*). The chromium in the filtered solution is reoxidised to chromate by adding a slight excess of sodium peroxide and then boiling well to decompose the excess of peroxide. The test is carried out on this solution as given above.

Vanadium.— Acidify a portion of the solution with sulphuric acid and precipitate molybdenum, if present, by hydrogen sulphide in a pressure flask (page 276). If tin be present, oxalic acid will keep it in solution. Molybdenum, arsenic and traces of platinum will be precipitated, if present. The filtrate from the precipitated sulphides is boiled while a current of carbon dioxide is passing through the solution in order to drive off the hydrogen sulphide. Evaporate the solution to dryness and remove the excess of sulphuric acid in an air bath. Dissolve the residue in water, and add a few drops of hydrogen

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[1] Note, zinc and chromates may form insoluble zinc chromate in alkaline solutions— G. Chancel, *Compt. rend.*, 43, 927, 1856.

[2] W. J. Karslake (*Journ. Amer. Chem. Soc.*, 31, 251, 1909) says that if hydrogen peroxide be added to the alkaline solution and the solution then acidified, the addition of ether is unnecessary except when very small traces of chromium are present. W. B. S. Bishop and F. P. Dwyer (*Journ. Proc. Australian Chem. Inst.*, 2, 278, 1935) advocate amyl acetate instead of ether.

[3] See A. Terni, *Gazz. Chim. Ital.*, 43, ii, 63, 1913. A. Terreil (*Bull. Soc. chim.*, (2), 3, 30, 1865; *Chem. News*, 11, 136, 1865) precipitates the chromium as lead chromate. This is all right if molybdenum, etc., are absent. W. Gibbs (*Amer. J. Science*, (2), 39, 59, 1865; (3), 5, 110, 1873; *Chem. News*, 28, 63, 1873) separates uranium from chromium quantitatively or qualitatively by boiling the solution with a slight excess of sodium hydroxide and then oxidising with bromine. The uranium will be found in the precipitate as sodium uranate, the chromium in the filtrate. If a little chromium be present in the precipitate, it can be removed by dissolving the precipitate in dilute nitric acid, boiling to expel nitrous fumes, and finally precipitating the chromium as mercurous or barium chromate.

[4] P. Cazeneuve, *Compt. rend.*, 131, 346, 1900; *Bull. Soc. chim.*, (3), 25, 758, 761, 1901; A. Moulin, *ib.*, (3), 31, 295, 1904; A. O. Snoddy, *Journ. Oil and Fat Ind.*, 2, 20, 1925; H. Spurrier, *Journ. Amer. Cer. Soc.*, 10, 330, 1927; W. W. Scott, *Standard Methods of Chemical Analysis*, New York, 1, 163, 1927; N. M. Stover, *Journ. Amer. Chem. Soc.*, 50, 2363, 1928; G. Sensi and R. Testori, *Ann. Chim. appl.*, 19, 383, 1929; H. Leitmeier and F. Feigl, *Tsch. Min. Petr. Mitt.*, 41, 95, 1931. P. N. van Eck (*Chem. Weekb.*, 12, 6, 1915) says that when a trace of α-naphthylamine is added to a solution of potassium dichromate, and the solution acidified with tartaric acid, an intense blue coloration is produced. For the detection of chromium by benzidine and o-tolidine, see L. M. Kul'berg, *Mikrochem.*, 20, 244, 1936.

peroxide. A characteristic "brick-red" coloration develops if vanadium be present.[1] The colour is bleached by the addition of an *excess* of hydrogen peroxide, an effect which is said to be inhibited by the addition of oxalic acid to the test solution. It is also stated that the colour given by molybdenum, if present, is entirely bleached by boric acid,[2] which does not affect the vanadium colour. In the presence of iron, the addition of 5 per cent. of phosphoric acid is recommended and the disturbing influence of titanium, when present, is counteracted by hydrofluoric acid.[3] Cupferron (ammonium nitrosophenyl-hydroxylamine) gives a red coloration or precipitate with vanadic acid[4] and this changes to green when the reagent is oxidised. The precipitation is not quantitative; as a colour test it will indicate one-millionth of a gram of vanadium per c.c.[5]

§ 255. The Separation of Chromium, Iron, Titanium, Aluminium, Vanadium and Uranium from Manganese, Cobalt, Nickel and Zinc.

Chromium in the Basic Acetate Separation.—In applying the basic acetate process, it may be remembered that both chromium acetate and chromium hydroxide are easily soluble in acetic acid. It might therefore be supposed that some of the chromium will be dissolved when the basic precipitation is made in the presence of free acetic acid. Some claim that practically all the chromium can be precipitated with the iron and aluminium, even in the presence of some free acetic acid, because the chromium acetate seems to assume a kind of "passive state" towards acetic acid, particularly when the chromium is in very large excess; but it is necessary to make sure the chromium has all been precipitated by adding hydrogen peroxide to the filtrate. A blue coloration shows that chromium is present in the filtrate.[6] Some recommend transforming the chromium salts into chromates before applying the basic acetate process. Most of the chromium then passes into the filtrate along with some of the aluminium as aluminium chromate, but a part remains with the precipitate in the form of basic chromates of iron and aluminium.[7]

[1] C. M. Johnson (*Rapid Methods for the Chemical Analysis of Special Steels*, New York, 5, 1909) states that ferrous ammonium sulphate will discharge the brick-red coloration of vanadium more quickly than the yellowish-orange tint of titanium compounds. Hence, if ferrous ammonium sulphate be added to a solution containing both vanadium and titanium in the presence of hydrogen peroxide, the brick-red colour will fade to a bright yellow tint before the colour is discharged: if titanium be absent, the brick-red coloration will fade to a colourless solution without showing the yellow tint. Fenton's reagent—page 519—gives better results in detecting titanium in the presence of vanadium. J. A. Pickard (*Chem. World*, 2, 341, 1913; A. Fölsner, *Chem. Ztg.*, 53, 259, 1929) claims that the turbidity given by lead acetate solution with a vanadate solution is much more delicate than the hydrogen peroxide test.

[2] J. Lukas and A. Jílek, *Zeit. anal. Chem.*, 76, 348, 1929.

[3] T. Gedeon, *Magyar Chem. Fol.*, 37, 89, 1931.

[4] V. G. Rodeja, *Anal. Fis. Quim.*, 12, 305, 1914; W. A. Turner, *Amer. Journ. Sci.*, (4), 41, 339, 1916; 42, 109, 1916.

[5] For the detection of vanadium by *strychnine*, see A. W. Gregory, *Proc. Chem. Soc.*, 25, 232, 1909; by *dimethylglyoxime*, F. Ephraim, *Helv. Chim. Acta*, 14, 1266, 1931; by *p-phenylenediamine hydrochloride*, D. Katakousinos, *Praktika*, 4, 448, 1931; *Chem. Zentr.*, (1), 845, 1932; by 5 : 7-*dibromo-8-hydroxyquinoline*, G. Gutzeit and R. Monnier, *Helv. Chim. Acta*, 16, 239, 1933.

[6] B. Reinitzer, *Monats.*, 3, 249, 1882; *Chem. News*, 48, 114, 1883; F. Mayer, *Ber.*, 22, 2627, 1889. One writer says: "The method of separating ferric and aluminium salts in the form of basic acetates entirely loses its applicability in the presence of chromium salts."

[7] H. Brearley, *Chem. News*, 76, 175, 1897; 77, 47, 179, 1898.

The error due to the formation of basic ferric chromates is least w█████ the precipitation of the iron from the chromate solution is made with sodium hydroxide in sufficient excess to decompose the basic ferric chromate. If but a small amount of iron be present, the excess need not be very large.[1] Sodium carbonate is quite as good provided also a sufficient excess be used. Thus Brearley [2] found that in a litre of solution containing 1 grm. of iron, and 0·375 grm. of potassium chromate, the addition of a varying excess of alkali led to the results shown on the left of Table LV.; and with solutions containing half a gram per litre of aluminium in place of iron and 0·2895 grm. of potassium chromate, a varying excess of alkali gave recoveries of chromium from the filtrate as shown on the right of the same table.

Table LV.—Effect of an Excess of Alkali on the Separation of Iron, Aluminium and Chromium.

Excess of alkali 2N-sol.	Percentage recovery of chromium from filtrate.			Excess of alkali 2N-sol.	Percentage recovery of chromium from filtrate.		
	Sodium carbonate.	Sodium hydroxide.	Ammonia.		Sodium carbonate.	Ammonium carbonate.	Ammonia.
0 c.c.	54·6	69·3	24·8	10 c.c.	94·0	81·3	89·0
10 ,,	90·4	100·0	70·4	20 ,,	95·3	93·6	90·5
20 ,,	97·5	99·8	77·0	30 ,,	99·0	94·4	93·1
30 ,,	98·7	100·0	83·6				
50 ,,	100·1	..	87·8				

The results show that sodium carbonate or sodium hydroxide gives good separations of iron from chromium if a sufficient excess be used. But when chromium is to be separated from aluminium, "one may therefore choose between leaving chromic acid in the precipitate or losing aluminium hydroxide in the filtrate" since the latter is redissolved by the excess of alkali.

Consequently, as indicated on page 383, avoid the basic acetate process for the separation of chromium from manganese, cobalt, nickel, zinc and ferrous salts. In many cases the chromium will be precipitated with the aluminium, iron and titanium both in the "basic acetate" and in the "ammonia" processes.[3] It then remains to separate the chromium from the iron, aluminium and titanium by some other process, say Knorre's method, or the mercurous nitrate process. If the ammonia precipitation be made by the simultaneous additions of bromine and ammonia to the hot solution, Jakób says that a good separation of aluminium and chromium can be obtained.[4]

The Barium Carbonate Method.—This method originated with Fuchs and Rose [5] and it is more satisfactory than the basic acetate process when chromium

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[1] Similar remarks apply to the separation of molybdenum by this process—F. Ibbotson and H. Brearley, *Chem. News,* 81, 269, 1900; 79, 3, 1899.

[2] H. Brearley, *Chem. News,* 76, 175, 1897; 77, 49, 131, 179, 216, 1898; W. Galbraith, *ib.,* 77, 187, 1898.

[3] It must be borne in mind that aluminium hydroxide and chromium hydroxide are slightly soluble in ammonia, so that the filtrate from the ammonia precipitate must be boiled to recover the aluminium and chromium, as indicated on page 535.

[4] W. Jakób, *Bull. Internat. Acad. Cracovie,* A, 56, 1913.

[5] J. N. von Fuchs (*Schweigger's Journ.,* 62, 184, 1831) also used calcium carbonate. H. Rose, *Pogg. Ann.,* 83, 137, 1851; J. F. W. Herschel, *Ann. Chim. Phys.,* (3), 49, 306, 1837; G. van. Pelt, *Bull. Soc. chim. Belg.,* 28, 101, 138, 1914; B. S. Evans, *Analyst,* 62, 363, 1937.

is present. The barium carbonate process depends upon the fact that ferric, aluminium, chromium, vanadium, titanium and uranium hydroxides are precipitated from cold dilute solutions in a few hours by barium carbonate, while manganese, nickel, cobalt, zinc and ferrous salts are not precipitated. The barium is subsequently removed from both the precipitate and filtrate.

Ferric salts, etc., are readily hydrolysed (pages 162 and 381) in aqueous solutions:

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl$$

In the presence of barium carbonate, the free acid will be removed as fast as it is formed: $BaCO_3 + 2HCl = BaCl_2 + H_2O + CO_2$; equilibrium is disturbed; and the hydrolysis is completed. The net result of the action is represented by the equation:

$$2FeCl_3 + 3H_2O + 3BaCO_3 = 3BaCl_2 + 2Fe(OH)_3 + 3CO_2$$

If the solution be heated, the salts of zinc, nickel, etc., may also be hydrolysed, and, in consequence, precipitated by the barium carbonate treatment. If much nickel and cobalt be present, small amounts of these elements will be precipitated by the barium carbonate even in the cold. The presence of ammonium chloride,[1] however -- about 5 grms. per 100 c.c. of solution—prevents the precipitation of nickel and cobalt, and the results are then quite satisfactory. The method has also been recommended for separating vanadium and chromium from *ferrous* iron [2] and manganese. With these elements, the separation is effected after a few minutes' boiling with barium carbonate.[3] Mercuric oxide,[4] zinc hydroxide [5] and cadmium carbonate [6] have also been proposed in place of barium carbonate. The cadmium can be removed by subsequent treatment with hydrogen sulphide. The *modus operandi* is as follows:—

The slightly acid solution containing nitrates or chlorides of the elements indicated above, but free from sulphates,[7] is treated in an Erlenmeyer's flask with a solution of sodium carbonate, as in the basic acetate process, until a slight permanent turbidity is produced. This is cleared by a drop or two of dilute hydrochloric acid. The dilute solution is thoroughly agitated with an emulsion of barium carbonate (that is, barium carbonate suspended in water).[8] The flask is closed and allowed to stand several hours, with occasional shaking. Decant the clear solution through a filter-paper and wash the residue three times with cold water; transfer the precipitate to the filter-paper by means of cold water.

[1] P. Schwarzenberg, *Liebig's Ann.*, **97**, 216, 1856.

[2] It is almost impossible to prevent the precipitation of a little iron from "ferrous solutions," but the error from this effect is so small that C. R. Fresenius (*Quantitative Chemical Analysis*, London, **1**, 434, 1876) recommended the process in special cases for the separation of ferrous iron from ferric iron.

[3] A. Steffan, *Ueber die Bestimmung von kleinen Mengen an Chrom und Vanadin in Gestein und Stahlarten*, Zürich, 1902.

[4] J. J. Berzelius, *Lehrbuch der Chemie*, Dresden, **10**, 139, 145, 1826; J. Volhard, *Liebig's Ann.*, **198**, 331, 1879; C. Zimmermann, *ib.*, **232**, 273, 1886; C. Meineke, *Zeit. angew. Chem.*, **1**, 252, 1888; E. F. Smith and P. Heyl, *Zeit. anorg. Chem.*, **7**, 82, 1894.

[5] C. Meineke, *Zeit. angew. Chem.*, **1**, 252, 1888; P. Slawik, *Chem. Ztg.*, **34**, 648, 1910.

[6] J. R. Cain, *Bull. Bur. Standards*, **7**, 377, 1911.

[7] The solution must be quite free from sulphates, otherwise barium will be precipitated, *e.g.* $ZnSO_4 + BaCO_3 \rightleftharpoons ZnCO_3 + BaSO_4$.

[8] BARIUM CARBONATE.—The barium carbonate must be tested by dissolving a portion of it in hydrochloric acid and precipitating the barium by the addition of sulphuric acid; the filtrate must leave no residue when evaporated to dryness in a platinum dish, showing that the barium carbonate is free from alkali carbonates, etc.

(a) *The precipitate* is dissolved in hydrochloric acid, heated to boiling to remove the carbon dioxide and the iron, vanadium, chromium, aluminium, titanium and uranium are either precipitated by ammonium sulphide, or the barium is removed by means of sulphuric acid or sodium sulphate. The latter process is not so good as the former, because the barium sulphate is liable to carry down some of the metals from the solution.

(b) *The filtrate* from the barium carbonate is heated to boiling and treated with sulphuric acid or sodium sulphate to precipitate the barium. The precipitate is washed. The filtrate contains manganese, cobalt, nickel, zinc and ferrous salts,[1] if present.

The main objection to the cold process—particularly with chromium—is the time required for the precipitation, and the subsequent removal of barium. The precipitation can, of course, be allowed to proceed overnight when the results are not urgently wanted. As indicated above, in the special case where chromium and vanadium have to be separated from manganese and ferrous salts, the solution can be heated to boiling and small additions of barium carbonate made every two or three minutes until an excess of about 1 to 2 grms.[2] has been added. After 10 to 15 minutes' boiling, let the mixture stand a few minutes to allow the precipitate to settle, filter and wash the residue with hot water. Place the filter-paper and precipitate in a large platinum crucible; burn off the filter-paper and fuse the residue with about 2 grms. of sodium carbonate and 0·25 grm. of sodium nitrite. The fused mass is extracted with water; any ferric oxide present remains undissolved, while sodium aluminate, chromate and vanadate pass into solution. The solution is treated with acetic acid and lead acetate, or with dilute nitric acid and lead nitrate, for the precipitation of lead chromate and lead vanadate, as indicated below.

§ 256. The Separation of Chromium and Vanadium in the Analysis of Silicates.

Decomposition of the Silicate.[3]—Fuse 5 grms. of the powdered sample with about 20 grms. of sodium carbonate and 3 grms. of sodium nitrite.[4] Extract with water; reduce the sodium manganate with a few drops of alcohol; nearly neutralise the solution with nitric acid—about 150 c.c. of acid (sp. gr. 1·05) will be needed. The solution must not be acid or nitrous acid will be liberated, and this, in turn, will reduce some of the chromium and some of the vanadium.[5] Evaporate the solution to dryness, take up the mass with water and filter. Ignite the precipitate; treat the ignited mass with

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[1] As a rule, the ferrous iron is oxidised to the ferric state, so that no iron remains in the filtrate.

[2] Too much barium carbonate makes the subsequent extraction of the chromium difficult.

[3] W. F. Hillebrand, *Amer. J. Science*, (4), 6, 210, 1898; *Chem. News*, 78, 216, 1898. The higher oxidation products—chromates—are not precipitated by ammonia. Hence the silicate can be decomposed with the sodium peroxide fusion in a nickel crucible and the cake taken up with hydrochloric acid. The silica is removed as usual. The alumina is precipitated by boiling the solution made alkaline with ammonia and hydrogen peroxide. The precipitate is washed with a solution of ammonium nitrate, redissolved and reprecipitated with ammonia and hydrogen peroxide as before. The alumina is then practically free from vanadium. The vanadium and chromium remain in the filtrate—W. Trautmann, *Stahl Eisen*, 30, 1802, 1910.

[4] E. Claassen (*Amer. Chem. Journ.*, 8, 437, 1886) shows that the undecomposed residue from some minerals requires re-fusion, since, if much vanadium be present and the vanadium is to be determined, the insoluble residue will always contain vanadium.

[5] The amount of acid required to neutralise 20 grms. of sodium carbonate can be determined by a blank test.

sulphuric and hydrofluoric acids; evaporate to dryness; fuse with sodium carbonate; take up the mass with water; almost neutralise with nitric acid; boil; filter and add the filtrate to the main solution. The object of this treatment is to recover chromium which is retained by the precipitated silica.

Precipitation of Chromium and Vanadium.—Add an almost neutral solution of mercurous nitrate [1] to the cold, barely alkaline solution until no further precipitation takes place. A bulky precipitate [2] containing mercurous carbonate, chromate and vanadate is obtained.[3] Boil; filter; wash with water containing a little mercurous nitrate or ammonium nitrate in solution; dry the precipitate and transfer as much as possible to a platinum crucible. Burn the filter-paper separately and add the ash to the main precipitate, which is ignited to remove the mercury. Fuse the residue with sodium carbonate, leach with water and filter the yellow solution of sodium chromate into a small flask—25-50 c.c. If chromium *alone* be present and the amount small, it is determined colorimetrically; if the amount be relatively large, it is determined volumetrically or gravimetrically. If *both* chromium and vanadium be present, they can be determined as described below, § 257 and § 262; or § 263.

Knorre's Process [4] for Separating Chromium.—Dissolve the "ammonia" precipitate in dilute sulphuric acid and add an excess of ammonium persulphate, with sufficient sulphuric acid to prevent the precipitation of basic ferric sulphate. On boiling, the dilute solution is converted into chromic acid. The iron and aluminium are then precipitated by ammonia in the usual manner. The precipitate is dissolved in dilute sulphuric acid and the operation is repeated so as to eliminate the trace of chromium precipitated with the aluminium and iron.[5] The chromium is determined in the joint filtrate in the

[1] Page 442. For the precipitation of vanadium as mercury vanadate, see C. R. von Hauer, *Journ. prakt. Chem.*, (1), 69, 385, 1856; C. Rammelsberg, *Ber.*, 1, 158, 1868; E. Claassen, *Amer. Chem. Journ.*, 7, 349, 1885; C. Radau, *Liebig's Ann.*, 251, 114, 1889; R. Holverscheit, *Ueber die quantitative Bestimmung des Vanadins und die Trennung der Vanadinsäure von Phosphorsäure*, Berlin, 10, 1890; S. Cinberg, *Journ. Russ. Met. Soc.*, 173, 1926; A. Jilek and J. Lukas, *Chem. Listy*, 24, 73, 1930. For the precipitation as silver orthovanadate, see L. Moser and O. Brandl, *Monats.*, 51, 169, 1929; as manganese vanadate, K. Swoboda and R. Horny, *Zeit. anal. Chem.*, 80, 271, 1930; M. E. Pozzi-Escot, *Compt. rend.*, 149, 1131, 1909; A. Carnot, *ib.*, 104, 1803, 1850, 1887; E. Cremer and B. Fetkenheuer, *Wiss. Veröff. Siemens-Konz.*, 5, 199, 1927. It was formerly the custom to add a slight excess of mercurous nitrate and then mercuric oxide to neutralise the excess of nitric acid which is present in the solution of mercurous nitrate; but W. F. Hillebrand (*l.c.*) has shown that the mercuric oxide is not necessary, since the basic mercurous carbonate is sufficient to remove the small quantity of free nitric acid introduced along with the mercurous nitrate. Chlorides should be absent, or vanadium may be lost during the subsequent ignition of the precipitate. E. B. Auerbach and K. Lange, *Zeit. angew. Chem.*, 25, 2522, 1912.
[2] If the precipitate is inconveniently large, cautiously add a little nitric acid and then a drop of mercurous nitrate to make sure that precipitation is complete.
[3] Tungsten, molybdenum, phosphorus and arsenic, if present, will be precipitated.
[4] G. von Knorre, *Zeit. angew. Chem.*, 16, 1097, 1903; G. van Pelt, *Bull. Soc. chim. Belg.*, 28, 101, 138, 1914; J. J. Lichtin, *Ind. Eng. Chem. Anal. Ed.*, 2, 126, 1930. Cf. F. C. T. Daniels, *Journ. Ind. Eng. Chem.*, 6, 658, 1914; M. Herschkowitch, *Zeit. anal. Chem.*, 59, 11, 1920. F. Bourion and A. Deshayes (*Compt. rend.*, 156, 1769, 1913; 157, 287, 1913) treat the mixture of iron, aluminium and chromium oxides with a slow current of chlorine gas, mixed with the vapour of sulphur dichloride, starting at about 200° and gradually passing to 650°. If over 30 per cent. of chromium be present, an equal volume of powdered ammonium sulphate is added to the mixed oxides. Of the volatile chlorides, the anhydrous chromic chloride is alone insoluble in water.
[5] R. B. Riggs (*Amer. J. Science*, (3), 48, 409, 1894; *Chem. News*, 70, 311, 1894; W. J. Sell, *ib.*, 54, 299, 1886; *Journ. Chem. Soc.*, 35, 292, 1879) digests the precipitate in 100 c.c. of water, 10 c.c. of hydrogen peroxide, and 1 grm. of sodium or potassium hydroxide. When effervescence has ceased, separate the ferric hydroxide by filtration. The filtrate contains aluminium and chromium (as chromate). Acidify with acetic acid, precipitate the aluminium with ammonia; and the chromium is determined in the filtrate either by the volumetric or

usual manner by volumetric or gravimetric processes—§§ 259, 260 and 261, pages 530 to 534; and the precipitate, containing the aluminium, titanium and iron, is treated as indicated on page 198.

§ 257. The Colorimetric Determination of Chromium.

A solution of an alkali chromate is yellow. The intensity of the colour is proportional to the amount of chromate in solution.[1] If a solution (standard solution) containing a known amount of chromate has the same tint as another solution of equal depth of liquid (test solution), it is assumed that both solutions have the same amount of the alkali chromate in solution.

Standard Solution of Potassium Chromate.—This is prepared by dissolving 0·5110 grm. of potassium chromate in a litre of water made alkaline with sodium carbonate. One cubic centimetre of this solution represents 0·0002 grm. of Cr_2O_3. Dilute, say, 10 c.c. of this solution to 100 c.c. and then pipette, say, 10 c.c. of this diluted solution into the right test glass of the colorimeter.

Test Solution.—This is prepared by concentrating the alkaline solution under investigation and making it up to a definite volume—25, 50 or 100 c.c.—such that its colour is weaker than the standard solution. Pour this solution into the left test glass of the colorimeter.

Comparison.—Dilute the standard solution with water from a burette until its tint is the same as the test solution. If the tint of the test solution be faint, Nessler's tubes may be used as in the determination of ammonia, where the solution is examined through a vertical column instead of horizontally.

EXAMPLE.—10 c.c. of the diluted standard chromate solution (containing 0·00002 grm. of Cr_2O_3 per c.c.) needed 48 c.c. of water to dilute its tint to that of 250 c.c. of the test solution obtained from 1 grm. of clay. Hence 58 c.c. of test solution contains 0·0002 grm. of Cr_2O_3, and thus 250 c.c. (1 grm. of clay) has $(250 \times 0·0002)/58 = 0·00086$ grm. of Cr_2O_3, that is, the sample has the equivalent of 0·086 per cent. of chromic oxide. The amount of chromic oxide can be deducted from the ammonia precipitate.

According to Horn,[2] the test is most sensitive when about 0·01 grm. to 0·02 grm. of chromium sesquioxide is present per litre of solution. Hillebrand and Lundell say that the method is reliable between concentrations of 0·01 and 0·1 grm. of chromium sesquioxide per litre and that less than 2 mgrms. of chromium sesquioxide in one gram of rock can be exactly determined. Dittrich asserts that the method is not sensitive when the amount of chromium falls below 2 mgrms.[3] The smallest amount of chromium which can be

gravimetric process. J. Clarke (*Journ. Chem. Soc.*, 63, 1082, 1893) added sodium peroxide until the solution was alkaline, instead of using hydrogen peroxide and sodium hydroxide— T. Poleck, *Chem. News*, 69, 285, 1894; O. Kassner, *Archiv Pharm.*, 232, 226, 1895; M. E. Pozzi-Escot, *Bull. Soc. chim.*, (4), 5, 558, 1909.

[1] L. L. de Koninck, *Pharm. Ztg.*, 78, 594, 1889; F. W. Richardson, W. Mann and W. Hanson, *Journ. Soc. Chem. Ind.*, 22, 614, 1903; W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, 167, 37, 1900; *Journ. Amer. Chem. Soc.*, 20, 454, 1898; *Chem. News*, 78, 227, 239, 1898; F. L. Langmuir, *Ueber die quantitative Bestimmung des Chroms auf gewichtsanalytischen und kolorimetrischen Wege*, Freiburg i. Br., 1906; M. Dittrich, *Zeit. anorg. Chem.*, 80, 171, 1913; O. Hackl, *Chem. Ztg.*, 44, 63, 1920; B. S. Evans, *Analyst*, 46, 38, 1921; W. W. Scott, *Standard Methods of Chemical Analysis*, New York, 1, 162, 1368 f., 1927; E. Fogel'son, *Zavodskaya Lab.*, 2, 33, 1933.

[2] D. W. Horn, *Amer. Chem. Journ.*, 35, 253, 1906; W. F. Hillebrand and G. E. F. Lundell *Applied Inorganic Analysis*, New York, 413, 761, 1929; M. Dittrich, *Zeit. anorg. Chem.*, 80, 171, 1913.

[3] For a colorimetric method based upon the colour produced by mixing diphenylcarbazide and chromic acid, see P. Cazeneuve, *Zeit. angew. Chem.*, 13, 958, 1900; *Bull. Soc. chim.*, (3), 25, 758, 1901; A. Moulin, *ib.*, (3), 31, 295, 1904; *Chem. News*, 89, 268, 1904; A. O. Snoddy, *Journ. Oil and Fat Ind.*, 2, 20, 1925; W. W. Scott, *Standard Methods of Chemical*

detected in distilled water is 0·000013 grm. per 100 c.c., but if the solution contains much less than about 0·004 grm. of chromic oxide, Cr_2O_3, per 100 c.c. the comparison is not satisfactory, and a greater quantity of the original sample must be taken.

Errors.—The following numbers represent the results which can be obtained with known mixtures:

Cr_2O_3 used .	.	8·88	8·88	8·88	8·88	11·67	6·34 mgrms.
Cr_2O_3 found	.	8·45	9·01	8·91	9·29	11·54	6·27 mgrms.
Error	.	− 0·43	+ 0·13	+ 0·03	+ 0·41	− 0·13	− 0·07 mgrm.

If vanadium be present, the solution can be reserved for the determination of vanadium by the volumetric process; if manganese be present, see page 408.

§ 258. The Analysis of Chromites and Chromic· Oxides.

In the analysis of chromite (chrome iron ore), and also of the ignited chromic oxides used as colouring agents, we have a special difficulty arising from the insolubility, or rather the extremely slow rate of solution, of the materials in acids. We therefore depend upon a preliminary fusion of the material with a suitable flux. Here again the action of the flux is often so slow that it is important to grind the materials under investigation to a very fine powder and heat the mixture for a comparatively long time. There is a wide choice in the selection of the flux.[1] Sodium peroxide is now in almost general use. Here

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Analysis, New York, **1**, 163, 1927; W. J. Agnew, *Analyst*, **56**, 24, 1931; Y. D. Gol'denberg, *Zavodskaya Lab.*, **3**, 506, 1934; D. Brard, *Ann. Chim. anal. Chim. appl.*, **17**, 201, 1935; E. B. Sandell, *Ind. Eng. Chem. Anal. Ed.*, **8**, 336, 1936. F. Garratt (*Journ. Ind. Eng. Chem.*, **5**, 298, 1913; F. W. Hall, *Chemist-Analyst*, **25**, 63, 1936) recommends the use of sodium 1 : 8-dihydroxynaphthalene-3 : 6-disulphonate.

[1] FLUXES FOR OPENING CHROMITE.—Numerous fluxes have been used for the chromite fusion (S. Rideal and S. Roseblum, *Chem. News*, **73**, 1, 1896; J. A. Müller, *Bull. Soc. chim.*, (4), **5**, 1133, 1909). For example: SODIUM HYDROXIDE ALONE (H. N. Morse and W. C. Day, *Amer. Chem. Journ.*, **3**, 163, 1881; *Chem. News*, **44**, 43, 1881; L. Duparc and A. Leuba, *Ann. Chim. anal.*, **9**, 201, 1904). POTASSIUM HYDROXIDE AND CHLORATE (H. Schwarz, *Liebig's Ann.*, **69**, 212, 1849; *Zeit. anal. Chem.*, **22**, 83, 530, 1883; H. Pellet, *Berg. Hütt. Ztg.*, **40**, 224, 1881). MAGNESIA OR LIME WITH CAUSTIC SODA (J. Clark, *Journ. Soc. Chem. Ind.*, **11**, 501, 1892; *Chem. News*, **24**, 286, 304, 1871; A. Christomanos, *Ber.*, **10**, 16, 364, 1877; *Zeit. anal. Chem.*, **17**, 244, 1878; P. Vekšin, *Berg. Journ.*, **4**, 437, 1908; J. Clouet, *Dingler's Journ.*, **193**, 33, 1869; *Zeit. anal. Chem.*, **17**, 244, 1878; W. Herwig, *Stahl Eisen*, **36**, 646, 1916). *Clark's flux* is 1 part of the sample with 8 parts of a mixture of 5 parts of sodium hydroxide and 3 of calcined magnesia—heat in a Bunsen flame in a platinum crucible for about 40 minutes; WITH CALCIUM CHLORIDE (J. Massignon, *Journ. Anal. App. Chem.*, **5**, 465, 1891; J. Massignon and E. Watel, *Bull. Soc. chim.*, (3), **5**, 371, 1891); WITH SODIUM CARBONATE (R. Kayser, *Zeit. anal. Chem.*, **15**, 187, 1876); WITH A MIXTURE OF SODIUM AND POTASSIUM CARBONATES (J. E. Stead, *Journ. I. S. Inst.*, **43**, 160, 1893). Stead's mixture is sometimes called the *tribasic flux*—4 parts lime, 1 sodium carbonate, 1 potassium carbonate. It resembles *Kayser's flux*—2 parts of sodium carbonate, and 3 parts of lime; WITH BORAX (R. Fieber, *Chem. Ztg.*, **24**, 333, 1900; R. W. E. MacIvor, *Chem. News*, **82**, 97, 1900). SODA LIME AND SODIUM NITRATE (F. Calvert, *Dingler's Journ.*, **125**, 466, 1852; J. Fels, *ib.*, **224**, 86, 1877); AND POTASSIUM CHLORATE (C. Reinhardt, *Chem. Ztg.*, **13**, 430, 1889; J. B. Britton, *Chem. News*, **21**, 266, 1870; *Zeit. anal. Chem.*, **9**, 487, 1870; J. Fels, *ib.*, **18**, 498, 1879); AND BORAX GLASS (L. Perl and V. Stefko, *Stahl Eisen*, **24**, 1373, 1904). SODIUM PEROXIDE (W. Hempel, *Zeit. anorg. Chem.*, **3**, 193, 1893; H. K. Tompkins, *Chem. News*, **68**, 136, 1893; J. Clark, *Journ. Chem. Soc.*, **63**, 1079, 1893; E. H. Saniter, *Journ. I. S. Inst.*, **48**, 153, 1895; *Journ. Soc. Chem. Ind.*, **15**, 156, 1896; S. Rideal and S. Roseblum, *ib.*, **14**, 1017, 1895; C. Glaser, *Journ. Amer. Chem. Soc.*, **20**, 130, 1898; *Chem. News*, **77**, 123, 1898; G. Tate, *ib.*, **80**, 235, 1899; T. Poleck, *Ber.*, **27**, 1051, 1894; O. Kassner, *Arch. Pharm.*, **232**, 226, 1894; A. F. MacFarland, *Met. Chem. Eng.*, **15**, 279, 1916; P. Koch, *Chem. Ztg.*, **41**, 64, 1917; *Chem. Zentr.*, (1), 532, 817, 1917; *Stahl Eisen*, **36**, 1093, 1916; **37**, 266, 1917; W. Herwig, *ib.*, **36**, 646, 1916; A. J. Field, *Ind. Eng. Chem.*, **8**, 238, 1916; E. Little and

the action is quick, and the extreme care in grinding is not so very important as with less active fluxes. The fusion with sodium peroxide, or with a mixture of potassium hydroxide and sodium peroxide, can be made in a nickel, iron,[1] copper or silver [2] crucible. Platinum crucibles should not be used with caustic

J. Costa, *ib.*, **13**, 228, 1921; T. R. Cunningham and T. R. McNeill, *ib.*, *Anal. Ed.*, **1**, 70, 1929; J. Moir, *Journ. S. African Assoc. Anal. Chemists*, **2**, (1), 9, 1919; A. Franke and R. Dworzak, *Zeit. angew. Chem.*, **39**, 642, 1926; M. Berthet, *Chim. et Ind.*, Special No., 133, 1928; I. Majdel, *Arhiv. hem. Farm.*, **4**, 8, 1930; D. Millin, *S. African Journ. Science*, **31**, 177, 1934; F. H. Norton, *Refractories*, New York, 510, 1931; H. Fresenius and H. Bayerlein, *Zeit. anal. Chem.*, **37**, 31, 1898; E. Dittler, *Tsch. Min. Petr. Mitt.*, **40**, 189, 1929—using silver crucible); WITH SODIUM CARBONATE (L. Lucchese, *Ann. Chim. anal. Chim. app.*, **9**, 450, 1908; M. Höhnel, *Archiv Pharm.*, **232**, 222, 1886; C. Glaser, *Chem. Ztg.*, **18**, 1448, 1894; M. Berthet, *Monit. Produit Chim.*, **18**, 3, 1936; *Ceram. Abs.*, **16**, 45, 1937); WITH SODIUM NITRATE AND SODIUM CARBONATE (J. A. Müller, *Bull. Soc. chim.*, (4), **5**, 1133, 1909). OR SODIUM HYDROXIDE (J. Spuller and S. Kalman, *Chem. Ztg.*, **17**, 880, 1207, 1412, 1893; S. R. Scholes, *Glass Ind.*, **11**, 137, 1930; W. Dederichs, *Pharm. Ztg.*, **58**, 446, 1913). POTASSIUM PEROXIDE AND SODIUM CARBONATE (J. A. Müller, *Bull. Soc. chim.*, (4), **5**, 1133, 1909). BARIUM PEROXIDE (E. Donath, *Dingler's Journ.*, **263**, 245, 1887); WITH SODIUM CARBONATE (L. P. Kennicut and G. W. Patterson, *Journ. Anal. Chem.*, **3**, 131, 1889). POTASSIUM CARBONATE WITH SODIUM HYDROXIDE (C. Hausermann, *Chem. Ztg.*, **15**, 1601, 1891); WITH SODIUM CARBONATE AND BORAX (W. Dittmar, *Exercises in Quantitative Analysis*, Glasgow, 128, 1887; *Dingler's Journ.*, **221**, 450, 1878; P. Hart, *Journ. prakt. Chem.*, (1), **67**, 320, 1856; E. Waller and H. T. Vulte, *Chem. News*, **66**, 17, 1892; O. Nydegger, *Zeit. angew. Chem.*, **24**, 1163, 1911; T. R. Cunningham and T. R. McNeill, *Ind. Eng. Chem. Anal. Ed.*, **1**, 70, 1929). SODIUM CARBONATE AND POTASSIUM CHLORATE (R. Fresenius and E. Hintz, *Zeit. anal. Chem.*, **29**, 29, 1890). AMMONIUM NITRATE AND CAUSTIC SODA (C. A. Burghardt, *Chem. News*, **61**, 260, 1890). POTASSIUM BISULPHATE (E. Clark, *Journ. Amer. Chem. Soc.*, **17**, 327, 1895; H. Tamm, *Chem. News*, **24**, 307, 1871; C. L. Oudesluys, *ib.*, **5**, 255, 1862; C. O'Neill, *ib.*, **5**, 199, 1862; F. A. Genth, *ib.*, **6**, 30, 1862; *Zeit. anal. Chem.*, **1**, 498, 1862; W. Gibbs, *ib.*, **3**, 328, 1864; R. Namais, *Stahl Eisen*, **10**, 977, 1890; T. S. Hunt, C. O'Neill and F. A. Genth, *Amer. J. Science*, (3), **5**, 418, 1873), 1 part sample with 15 parts of potassium bisulphate; WITH SODIUM FLUORIDE OR CRYOLITE (H. Hager, *Untersuchungen*, Leipzig, **1**, 263, 1888; P. C. Dubois, *Zeit. anal. Chem.*, **3**, 401, 1864; S. Kern, *Chem. News*, **35**, 107, 1877; F. W. Clarke, *ib.*, **17**, 232, 1868; *Amer. J. Science*, (2), **45**, 173, 1868); AND SODIUM NITRATE (H. Rose, *Ausführliches Handbuch der analytischen Chemie*, Braunschweig, **2**, 376, 1851). POTASSIUM HYDROXIDE AND THE ELECTRIC CURRENT (E. F. Smith, *Ber.*, **24**, 2182, 1891). HYDROCHLORIC ACID UNDER PRESSURE (P. Jannasch and H. Vogtherr, *Ber.*, **24**, 3206, 1891). HEATING IN CURRENT OF CHLORINE, etc. (R. Fresenius and E. Hintz, *Zeit. anal. Chem.*, **29**, 28, 1890). HEATING WITH BROMINE WATER IN SEALED TUBES some days (E. F. Smith, *Amer. J. Science*, (3), **15**, 198, 1877); WITH SULPHURIC ACID (A. Mitscherlich, *Journ. prakt. Chem.*, (1), **81**, 108, 1860; (1), **83**, 455, 1861; *Zeit. anal. Chem.*, **1**, 54, 1862; F. C. Philips, *ib.*, **12**, 189, 1873; J. Jones, *Chem. News*, **65**, 8, 1892). TREATMENT WITH A MIXTURE OF POTASSIUM CHLORATE AND NITRIC OR SULPHURIC ACID. This is not particularly suited for chromites, but it is satisfactory for some chromic oxides (F. H. Storer, *Proc. Amer. Acad.*, **4**, 352, 1869; *Chem. News*, **21**, 195, 1870; C. Brunner, *ib.*, **4**, 57, 1861; A. H. Pearson, *Amer. Journ. Sci.*, (2), **48**, 190, 1869; H. Baubigny, *Bull. Soc. chim.*, (2), **12**, 291, 1884; B. Pawolleck, *Ber.*, **16**, 3008, 1883; T. R. Cunningham and T. R. McNeill, *Ind. Eng. Chem. Anal. Ed.*, **1**, 70, 1929; P. I. Dolinskil, *Zavodskaya Lab.*, **6**, 225, 1937).

[1] H. N. Morse and W. C. Day, *Amer. Chem. Journ.*, **3**, 163, 1881.

[2] All these crucibles are attacked. Porcelain may last from two to four times before it is cut through by the flux. Silver crucibles lose about half a gram per fusion. There is a danger in the use of silver crucibles from the fact that the crucible can be melted if heated at too high a temperature on the Bunsen flame. Silver, copper and lead may be found in the fusion after using a silver crucible—W. Dittmar, *Chem. Ztg.*, **15**, 1521, 1580, 1891. W. Bettel (*Chem. News*, **43**, 94, 1881) recommended a platinum crucible gilded inside for fusions with alkalies. See also J. L. Smith, *Chem. News*, **31**, 55, 1875. A. J. Field (*Journ. Ind. Eng. Chem.*, **8**, 238, 1916) uses a platinum crucible, placed inside a larger porcelain crucible heated by a small flame. Gold crucibles would be cheaper, in view of the higher price of platinum. Nickel crucibles are generally used. They lose about 0·1 grm. per fusion under the conditions described in the text. A crucible is said to last 15–25 fusions after a little practice in its use—but this estimate is rather high. Gold is not attacked *chemically* by fused potassium hydroxide, but nickel forms nickel hydroxide—M. le Blanc and O. Weyl, *Ber.*, **45**, 2300, 1912. See W. Dittmar and D. Prentice (*Journ. Soc.*

alkalies. If iron and chromium are alone to be determined, a porcelain crucible may be used. The procedure (nickel crucible) is as follows :—

Sodium Peroxide Fusion.—Grind the substance to a fine impalpable powder in an agate mortar, and, by means of a platinum or nickel spatula, intimately mix 0·5 grm. of the dry (110°) powder with about 4 to 5 grms. of sodium peroxide [1] in, say, a *pure* nickel crucible of not less than 50 c.c. capacity, and fitted as described on page 265. Heat the crucible gently over the tip of a Bunsen flame until the contents of the crucible are fluid—this takes about 10 minutes. Raise the temperature to low redness—say another 10 minutes. Cool. Place the crucible in a beaker (400 c.c.), cover the crucible with a clock-glass, and gradually add about 50 c.c. of cold water in such a way that the first addition of water flows slowly between the clock-glass and the crucible. The mixture bubbles up and dissolves in a few minutes.[2] Remove the crucible and rinse it carefully with water. Boil the solution about 10 minutes to decompose the sodium peroxide.[3] The oxides of iron, manganese, cobalt and nickel (mainly from the crucible) remain as insoluble residue. The chromium, aluminium and most of the silica, with a little magnesia and lime, pass into solution.

Set the beaker aside for a few minutes until the insoluble residue has thoroughly settled. Filter as much as possible of the supernatant liquid through a filter-paper,[4] then transfer the residue from the beaker to the filter-paper and repeatedly wash both the residue and paper with small quantities of hot, distilled water until the washings are colourless. Cool to room temperature and make the filtrate and washings up to 250 c.c. (or, if necessary, to 500 c.c.) in a graduated flask; finally shake well.[5]

Chem. Ind., **12**, 248, 1893) for the action of fused alkali hydroxides on gold and silver crucibles. Gold is scarcely attacked by a 10 minutes' fusion; silver is very little attacked by soda, rather more so by potash. Some use copper crucibles. The contamination from copper crucibles is said to give least trouble in many complex analyses. H. N. Morse and W. C. Day (*Amer. Chem. Journ.*, **3**, 163, 1881) recommended an iron crucible, provided iron has not to be determined. W. L. Dudley, *Amer. Chem. Journ.*, **28**, 59, 1902; Noaillon, *Bull. Soc. chim. Belg.*, **28**, 212, 1914; T. R. Cunningham and T. R. McNeill, *Ind. Eng. Chem. Anal. Ed.*, **1**, 70, 1929; J. Moir, *Journ. S. African Assoc. Anal. Chemists*, **2**, (1), 9, 1919.

[1] Reject the crust, if any, formed at the top of the peroxide bottle. This is mainly carbonate and oxide. L. Archbutt (*Analyst*, **20**, 3, 1895) reports a sample of sodium peroxide with 0·5 per cent. of alumina and ferric oxide.

[2] Sometimes it requires warming. If any of the residue be insoluble in dilute sulphuric acid (1 : 4), this means that some of the substance has not been decomposed. In that case the portion not dissolved must be re-fused with the flux. If nitric acid be used to take up the cake, some chromate may be reduced by the acid. A. Leuba, *Ann. Chim. anal. app.*, **9**, 303, 1908. Note the formation of volatile chromyl chloride when sulphuric acid is heated with a chloride and a chromate.

[3] To ensure the decomposition of the peroxide, some here recommend an evaporation to dryness. Peroxides must be absent in order to prevent reducing the chromates to chromic oxide—Cr_2O_3—when the solution is acidified. If the solution is purple-coloured, add a gram of sodium peroxide, and boil another 10 minutes.

[4] It is advisable to use a good grade, gravimetric paper (see page 78). A Whatman No. 54 hardened paper serves the purpose excellently, but see page 531.

[5] J. Moir (*Journ. S. African Assoc. Anal. Chemists*, **2**, (1), 9, 1919) says that the usual methods of fusion lead to errors, generally negative, which may amount to 10 per cent. of the chromium present, and recommends the following procedure. After fusion and extraction, add enough 20 per cent. sulphuric acid to effect solution. Then add 2 grms. of potassium persulphate or 3 to 5 grms. of the ammonium salt, warm rapidly to 80°, then gently to boiling. Remove the excess of persulphate by diluting the liquid with about 25 per cent. of its bulk of 20 per cent. sulphuric acid and boiling for 30 minutes. Cool and dilute to a definite volume.

§ 259. The Volumetric Determination of Chromium.

Determine the chromium in an aliquot portion of the above solution as follows.[1] Pipette out 25 c.c. of the chromate solution, add about 25 c.c. of 25 per cent. sulphuric acid and into the mixture pipette 25 c.c. of approximately 0·1N-ferrous ammonium sulphate solution.[2] Titrate the solution with 0·1N-potassium permanganate solution [3] until a faint pink colour appears. Now pipette out 25 c.c. of the ferrous ammonium sulphate solution, add about 25 c.c. of 25 per cent. sulphuric acid and titrate with the standard permanganate solution.

It is advisable to carry out both sets of titrations in triplicate and use the average of the readings in each series in the subsequent calculation. Assuming that the permanganate solution is exactly decinormal, the percentage of chromium sesquioxide is given by $15\cdot2\ v/3$ where v is the difference between the burette readings in the two titrations; hence a variation of $\pm0\cdot1$ c.c. in v means a difference of $\pm0\cdot5$ in the reported percentage of chromium sesquioxide in the sample.[4]

The respective reactions involved in the process are represented by:—

$$\text{(i)} \quad Cr_2O_3 + 3Na_2O_2 = 2Na_2CrO_4 + Na_2O$$
$$\text{(ii)} \quad 2Na_2CrO_4 + H_2SO_4 = Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$
$$\text{(iii)} \quad Na_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 = Na_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$$

We have now sufficient data to calculate the amount of chromium as chromic acid in the aliquot portion taken from the standard flask. Every gram of ferrous ammonium sulphate oxidised represents 0·06461 grm. of chromium sesquioxide—Cr_2O_3; or 0·08501 grm. of chromium trioxide—CrO_3.[5]

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[1] H. Schwarz, *Zeit. anal. Chem.*, **22**, 530, 1883; H. Bollenbach, *Chem. Ztg.*, **31**, 760, 1907; H. Vignal, *Bull. Soc. chim.*, (2), **45**, 171, 1886; *Chem. News*, **53**, 195, 1886; T. W. Hogg, *Journ. Soc. Chem. Ind.*, **10**, 340, 1891; R. L. Leffler, *Chem. News*, **77**, 156, 1898; W. Galbraith, *ib.*, **35**, 151, 1877; **77**, 187, 1898; A. Kurtenacker, *Zeit. anal. Chem.*, **52**, 401, 1913; F. Bourion and A. Sénéchal, *Compt. rend.*, **157**, 1528, 1913; G. Giorges, *Gazz. Chim. Ital.*, **23**, (1), 277, 1893; C. van Brunt, *Journ. Amer. Chem. Soc.*, **36**, 1426, 1914; G. L. Kelley and J. H. Connant, *ib.*, **38**, 716, 1916; F. C. T. Daniels, *Journ. Ind. Eng. Chem.*, **6**, 658, 1914; T. R. Cunningham and T. R. McNeill, *ib.*, *Anal. Ed.*, **1**, 70, 1929; W. Herwig, *Stahl Eisen*, **36**, 646, 1916; G. Schumacker, *ib.*, **36**, 1093, 1916; P. Koch, *ib.*, **36**, 1093, 1916; **37**, 266, 1917; *Chem. Ztg.*, **41**, 64, 1917; J. C. Bencker, *Chemist-Analyst*, **19**, 22, 1916; J. Moir, *Journ. S. African Assoc. Anal. Chemists*, **2**, (1), 9, 1919; A. Franke and R. Dworzak, *Zeit. angew. Chem.*, **39**, 642, 1926; E. Dittler, *ib.*, **39**, 279, 1926; W. Hild, *Chem. Ztg.*, **46**, 702, 1922; **55**, 895, 1931; A. and H. Eder, *ib.*, **46**, 1085, 1922; H. Mende, *ib.*, **53**, 178, 1929; W. Brüggemann, *ib.*, **53**, 927, 947, 1929; H. H. Willard and P. Young, *Ind. Eng. Chem. Anal. Ed.*, **6**, 48, 1934; A. Kopman, *Zavodskaya Lab.*, **3**, 464, 1934.

[2] FERROUS AMMONIUM SULPHATE SOLUTION.—Weigh out about 10 grms. of the finely powdered salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$, and dissolve in 150 c.c. of cold, distilled water, containing 10 c.c. of concentrated sulphuric acid. Dilute to 250 c.c.

[3] The titre of the permanganate solution should be checked against 0·1N-dichromate.

[4] VALUATION OF CHROME IRON ORES.—Chrome iron ores are valued on their Cr_2O_3 contents. The market value fluctuates. The standard for high-grade, hand-picked, cobbed ores is 50 per cent. Cr_2O_3, with a premium of, say, 2s. per unit per ton over 50 per cent., and a deduction of, say, 2s. per unit below 48 per cent. Cr_2O_3. Second-grade ores are referred to a 45 per cent. standard, with a premium of, say, 2s. per unit up to 48 per cent. Cr_2O_3. Ores carrying between 40 and 45 per cent. Cr_2O_3 inclusive are third-grade ores. The standard is 40 per cent. Cr_2O_3, and a premium or deduction is allowed for every unit above or below this standard. The so-called "concentrates" are divided into first and second grades; the former are referred to the 50 per cent. standard and the latter to the 45 per cent. standard, with premiums and deductions as before. Much crude ore is sold for furnace linings for steel furnaces. A maximum of 5 per cent. silica was formerly allowed, but ores with 8 per cent. of silica now find a market in the chromite brick industry.

[5] This process can also be used for evaluating alkali chromates and dichromates.

Error due to the Filtration of Chromate Solutions through Filter-Paper.[1]—If chromate solutions be filtered through paper, low results may be obtained owing to a partial reduction of the chromate. This error can be avoided by filtering the solution through asbestos, or by oxidising the solution *after* the filtration. The effect is produced by both acid and alkaline solutions; it is more marked with hot than with cold solutions; and also more marked with the lower-grade papers. For instance, 200 c.c. of a solution containing the equivalent of 25 c.c. of potassium dichromate (1 c.c. = 0·01 grm. Fe) were digested for half an hour with a 12·5 cm. filter-paper. In one case 50 c.c. of N-NaOH were added to the solution and in another case 50 c.c. of N-H$_2$SO$_4$. The results are shown in Table LVI.

Table LVI.—Effect of Filter-Paper on Chromate Solutions.

Filter-paper.	Ash of filter-paper.	C.c. of K$_2$Cr$_2$O$_7$ in filtrate.			
		Hot (100°).		Cold.	
	Grms.	Acid.	Alkaline.	Acid.	Alkaline.
Munktell's Swedish . .	0·0005	24·6	24·9	..	..
Schleicher and Schülls' 589	0·0003	23·8	24·2	25·0	25·0
Ordinary English . .	0·0028	23·6	24·6	25·0	25·0
French grey . . .	0·0139	22·5	24·0	24·0	24·7

The error with the ordinary filtration of chromate solutions may be equivalent to just over 0·1 per cent. of chromium.

The residue on the filter-paper can be dissolved in dilute sulphuric acid (1 : 4)[2] and the iron determined by titration (page 180). The result is usually calculated to FeO. If a complete analysis is needed, another peroxide fusion is made and dissolved in dilute hydrochloric acid. The silica is removed in the usual way and, after reduction of the chromate (see § 261), a double precipitation is made of the mixed oxides of chromium, iron and aluminium in an aliquot portion of the filtrate from the silica. Manganese, if present, will be in the filtrates from the ammonia precipitations. The amount of alumina is obtained by difference from the weight of the mixed oxides of chromium, iron and alumina. Another aliquot portion of the filtrate is used for the determination of sulphur. Lime, magnesia and manganese can be determined by the methods of pages 202, 208 and 397.[3]

An alternative volumetric procedure[4] is to take an aliquot portion of the

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[1] H. Jervis, *Chem. News*, 77, 133, 1898; A. Allison, *ib.*, 96, 1, 1907; R. S. McBride and J. A. Scherrer, *Journ. Amer. Chem. Soc.*, 39, 928, 1917. Compare R. W. Curtis and J. Finkelstein, *Ind. Eng. Chem. Anal. Ed.*, 5, 318, 1933.

[2] If any remain undissolved, the original fusion was not complete.

[3] For the complete analysis of chromites, see M. Berthet, *Chim. et Ind.*, Special No., 133, 1928; I. Majdel, *Arhiv. hem. Farm.*, 4, 8, 1930.

[4] K. Zulkowski, *Journ. prakt. Chem.*, (1), 103, 351, 1868; E. Walter, *Journ. Soc. Chem. Ind.*, 15, 436, 1896; J. Spüller and A. Brenner, *Chem. Ztg.*, 21, 3, 1897; J. A. Muller, *Bull. Soc. chim.*, (4), 3, 1133, 1908; (4), 5, 1133, 1909; A. J. Field, *Journ. Ind. Eng. Chem.*, 8, 238, 1916; E. Little and J. Costa, *ib.*, 13, 228, 1921; K. Schorlemmer, *Collegium*, 371, 1917; 145, 1918; A. Terni and P. Malaguti, *Gazz. Chim. Ital.*, 49, (1), 251, 1919; E. Müller

chromate solution, obtained as given above, and acidify it. 10 c.c. of a 10 per cent. solution of potassium iodide or 1-2 grms. of the solid salt are added and the liberated iodine is titrated with a standard solution of sodium thiosulphate, starch being added towards the end of the titration.[1] The reactions involved are :—

$$2Na_2CrO_4 + 2HCl = Na_2Cr_2O_7 + 2NaCl + H_2O$$
$$Na_2Cr_2O_7 + 6KI + 14HCl = 3I_2 + 2NaCl + 2CrCl_3 + 6KCl + 7H_2O$$
$$3I_2 + 6Na_2S_2O_3 = 6NaI + 3Na_2S_4O_6$$

Thus 6 grm.-molecules of sodium thiosulphate are equivalent to 2 grm.-molecules of sodium chromate, which are in turn produced from 1 grm.-molecule of chromium sesquioxide. Hence each c.c. of 0·1N-sodium thiosulphate used in the titration represents 0·002534 grm. of chromium sesquioxide, Cr_2O_3.

§ 260. The Gravimetric Determination of Chromium as Barium Chromate.

The Solubility of Barium Chromate.—This process [2] is based on the sparing solubility of barium chromate in water. One part of the salt has been variously reported as dissolving in from 87,000 to 300,000 parts of cold, and in 23,000 parts of boiling water.[3] The presence of acetic acid increases the solubility of the chromate; thus, 1 part of the salt dissolves in 37,000, 3670 and 1990 parts respectively of 1, 5 and 10 per cent. acetic acid. The presence of ammonium salts also makes the salt more soluble. For instance, 1 part of barium chromate dissolves in about 23,000 parts of water containing 0·5 per cent. of ammonium chloride; in 45,000 parts of water containing 0·5 per cent. of ammonium nitrate; in 50,000 parts of water containing 0·75 per cent. of ammonium acetate; and in 24,000 parts of a 1·5 per cent. solution of ammonium acetate. Hence the solution in which the precipitation is made must be but faintly acid with acetic acid. Mineral acids should be absent, or, if present, nearly neutralised by the addition of sodium carbonate, followed by sodium acetate.[4] Sulphuric acid or sulphates obviously must be absent.

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and W. Messe, *Zeit. anal. Chem.*, **69**, 165, 1926; E. Schulek and A. Dózsa, *ib.*, **86**, 81, 1931; F. L. Hahn, *ib.*, **97**, 305, 1934; *Journ. Amer. Chem. Soc.*, **57**, 614, 1935; A. Franke and R. Dworzak, *Zeit. angew. Chem.*, **39**, 642, 1926; G. Sirois, *Chemist-Analyst*, **17**, 10, 1928; E. Dittler, *Zeit. angew. Chem.*, **39**, 279, 1926; **41**, 132, 1928; *Tsch. Min. Petr. Mitt.*, **40**, 189, 1929; S. R. Scholes, *Glass Ind.*, **11**, 137, 1930; P. Klinger, *Stahl Eisen*, **50**, 1166, 1930; *Arch. Eisenhüttenw.*, **4**, 7, 1930–31; J. H. van der Meulen, *Rec. Trav. chim.*, **51**, 369, 1932; W. Erhard, *Mitt. Fors. Gutehoffnungshütte-Konz.*, **2**, 268, 1934; L. Crismer, *Ber.*, **17**, 642, 1884; J. Waddell, *Analyst*, **43**, 287, 1918; W. Dederichs, *Pharm. Ztg.*, **58**, 446, 1913; H. J. Taverne, *Chem. Weekb.*, **20**, 210, 1923. *Cf.* G. F. Smith and C. A. Getz, *Ind. Eng. Chem. Anal. Ed.*, **9**, 378, 1937.

[1] K. Schorlemmer (*l.c.*) and A. Franke and R. Dworzak (*l.c.*) state that the chromate solution must be free from all iron salts. Compare C. C. Benson, *Journ. Phys. Chem.*, **7**, 356, 1903.

[2] G. Chancel, *Compt. rend.*, **43**, 927, 1856 ; W. Gibbs, *Zeit. anal. Chem.*, **12**, 309, 1873; A. H. Pearson, *Amer. Journ. Sci.*, (2), **48**, 198, 1869; A. J. Field, *Journ. Ind. Eng. Chem.*, **8**, 238, 1916; L. W. Winkler, *Zeit. angew. Chem.*, **31**, 46, 1918; L. A. Congdon and R. K. Gurley, *Chem. News*, **128**, 68, 1924.

[3] R. Fresenius, *Zeit. anal. Chem.*, **29**, 418, 1890; **30**, 672, 1891; P. Schweitzer, *Zeit. anal. Chem.*, **29**, 414, 1890; F. Kohlrausch, *Zeit. phys. Chem.*, **64**, 121, 1908; I. Meschtschersky, *Journ. Russ. Phys. Chem. Soc.*, **14**, 219, 1882; *Zeit. anal. Chem.*, **21**, 399, 1882; J. Waddell, *Analyst*, **43**, 287, 1918; M. Lemarchands and M. Sirot, *Compt. rend.*, **194**, 1577, 1932.

[4] L. Schulerud, *Journ. prakt. Chem.*, (2), **19**, 36, 1890. Chlorides of ammonium, potassium, magnesium and calcium do not interfere; nitrates, chlorates and acetates give high results—L. W. Winkler, *Zeit. angew. Chem.*, **31**, 46, 1918.

Oxidation to Chromic Acid.—If the chromium be present in the lower state of oxidation, it must be converted into chromic acid by the addition of an oxidising agent. Hence warm the alkaline solution with a suitable oxidiser, *e.g.* sodium peroxide, or hydrogen peroxide,[1] or bromine,[2] or chlorine.[3] Nitric acid is rather slow in action.[4] Potassium chlorate acts fairly well in the presence of hydrochloric acid, but there is a difficulty in removing the last traces of chlorine oxides, especially in dilute solutions.[5] If the chromium be already present in the form of chromate, there is no need for the oxidation.

Precipitation of Barium Chromate.—If necessary, neutralise the solution with acetic acid.[6] Add a hot solution of barium acetate,[7] slowly, drop by drop,[8] to the hot neutral or weakly acidified solution. Let the mixture stand until cold; and, when the precipitate has settled, wash five times by decantation with hot water.[9] Filter [10] through asbestos felt in a Gooch crucible.[11] Wash the precipitate with dilute alcohol (alcohol 1 vol., water 10 vols.), and dry it in an air bath at $110°$.[12]

The Ignition.—Heat the covered crucible in a saucer, gently at first, and finally over the full flame of a Teclu burner. In about 5 minutes, remove the lid and heat the crucible until the precipitate has a uniform yellow colour.[13] Cool the crucible in a desiccator and weigh as barium chromate—$BaCrO_4$. Multiply the weight by exactly 0·3 to get the equivalent amount of chromium sesquioxide--Cr_2O_3.

Results.—Working with solutions containing the equivalent of 0·6886 grm. of $BaCrO_4$, the following numbers were obtained:

$BaCrO_4$	.	0·6922	0·6918	0·6876	0·6861	grm.
Error	.	+0·0036	+0·0032	−0·0010	−0·0025	grm.

[1] W. J. Sell, *Chem. News*, 54, 299, 1886; A. Carnot, *Compt. rend.*, 107, 997, 1888; F. Bourion and A. Sénéchal, *ib.*, 157, 1528, 1913; G. Sirois, *Chemist-Analyst*, 17, 10, 1928.

[2] Bromine is a favourite oxidising agent. It does not attack platinum. R. von Wagner, *Deut. Ind. Ztg.*, 19, 114, 1878; *Dingler's Journ.*, 218, 332, 1875; 219, 544, 1876; P. Waage, *Zeit. anal. Chem.*, 10, 206, 1871; *Chem. News*, 25, 282, 1872; H. Kämmerer, *Ber.*, 4, 218, 1871; E. Reichardt, *Arch. Pharm.*, (3), 5, 1, 1876; G. Vulpius, *ib.*, (3), 5, 422, 1876.

[3] W. Gibbs, *Amer. J. Science*, (2), 39, 58, 1865.

[4] If the solution also contains chlorides, nitric acid must not be used in a platinum dish.

[5] F. H. Storer (*Proc. Amer. Acad.*, 4, 342, 1869; *Amer. J. Science*, (2), 45, 190, 1868) used a mixture of potassium chlorate and nitric acid for oxidising chromium salts— B. Pawolleck, *Ber.*, 16, 3008, 1883. T. R. Cunningham and T. R. McNeill, *Ind. Eng. Chem. Anal. Ed.*, 1, 70, 1929, oxidise with a mixture of perchloric and sulphuric acids.

[6] For the reduction of chromic acid by acetic acid, see H. Basset, *Chem. News*, 79, 157, 1899; A. F. Leuba, *Ann. Chim. anal.*, 9, 303, 1904. "Small quantities of acetone, aldehyde, etc., are present in the inferior (grades of) acid."

[7] Barium nitrate or chloride give rather high results, and are not so satisfactory as the acetate—F. L. Langmuir, *Ueber die quantitative Bestimmung des Chroms auf gewichtsanalytischen und kolorimetrischen Wege*, Freiburg i. Br., 1906.

[8] If the barium acetate be added too quickly, barium acetate and other salts present in solution will be carried down with the chromate—R. H. Richards, *Chem. News*, 21, 198, 1870. For this reason M. Gröger (*Zeit. anorg. Chem.*, 81, 233, 1913) has reported adversely on the process.

[9] A. H. Pearson (*Amer. Journ. Sci.*, (2), 48, 198, 1869; *Chem. News*, 21, 198, 1870) recommends a solution of ammonium acetate for the washing, but the greater solubility of the precipitate in this menstruum must be taken into account.

[10] The precipitate is very awkward to filter through paper.

[11] Use very gentle suction. If strong suction be applied, the felt gets choked and subsequent filtration and washing will be very slow.

[12] It must be remembered that vanadium will be precipitated as barium vanadate, if this metal be present—A. Carnot, *Compt. rend.*, 104, 1803, 1887.

[13] The edges near the crucible sometimes appear green. This is due to a slight reduction by dust and alcohol. When heated in the open crucible, the green colour gradually disappears.

The precipitate may be dissolved in hydrochloric acid, mixed with a solution of potassium iodide and the liberated iodine titrated with sodium thiosulphate as indicated on page 531. Instead of barium acetate, lead, silver or mercurous nitrate may be used as precipitating agents. The precipitate is washed with a solution of the salt used for the precipitation. In the case of mercurous chromate, ignition converts the precipitate into chromium sesquioxide—Cr_2O_3.[1]

§ 261. The Gravimetric Determination of Chromium as Chromium Sesquioxide.

Chromium is most easily and quickly determined by volumetric methods. The gravimetric process is only used in special cases. If the chromium be in solution in the lower state of oxidation, it can be precipitated by the addition of a slight excess of ammonia in the presence of ammonium salts[2]; of freshly prepared ammonium sulphide to the boiling solution; or of hydrazine sulphate.[3] Filter, wash, calcine and weigh as chromium sesquioxide Cr_2O_3. Details of the procedure are as follows :—

Reduction of Chromates.—If chromates be present, they must be reduced to chromic salts. Boil the solution with 10 c.c. of hydrochloric acid and 10 c.c. of alcohol; and continue the boiling until all the alcohol has been expelled. Sulphurous acid and sulphites are also excellent reducing agents. Jannasch and Mai[4] reduce the solution by the addition of 5 c.c. of hydrochloric acid and a couple of grams of hydroxylamine hydrochloride. This, later on, facilitates the precipitation and washing. Slightly better results are obtained with sulphuric acid and hydroxylamine hydrochloride. Suppose that 25 c.c. of a solution of potassium chromate be under investigation, acidify the cold solution with 1 to 5 c.c. of dilute sulphuric acid,[5] and add 1 gram of hydroxylamine hydrochloride.[6]

The Precipitation.—Add a slight excess of ammonia,[7] and boil the solution to drive off the excess of ammonia. Filter quickly while still hot and wash with a dilute solution of ammonium nitrate as indicated for alumina (page 164).[8] The precipitate is dissolved in hydrochloric acid and again precipitated with ammonia as just described.

Ignition.—The wet precipitate is placed in a platinum crucible and the temperature gradually raised so as to prevent small particles of the precipitate

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[1] L. A. Congdon and R. K. Gurley (*Chem. News*, **128**, 68, 1924) say that this method gives low results as a small part of the chromate is reduced to the chromic salt and so escapes precipitation.

[2] M. Z. Jówitschitsch, *Monats.*, **34**, 225, 1913.

[3] T. Hanuš and T. Lukas, *Chem. Ztg.*, **36**, 1134, 1912.

[4] P. Jannasch and J. Mai, *Ber.*, **26**, 1786, 1893; P. Jannasch and F. Rühl, *Journ. prakt. Chem.*, (2), **72**, 10, 1905; C. Friedheim and P. Hasenclever, *Zeit. anal. Chem.*, **44**, 594, 1905.

[5] It is not advisable to use less than 1 c.c. of dilute sulphuric acid. If too little acid be used, the reduction is disturbed by a side reaction attended by the development of nitrous fumes, and the formation of a brown instead of a violet-coloured solution.

[6] The addition of 2 c.c. of a 2·5 per cent. solution of tannin before the addition of the ammonia gives a precipitate much easier to filter and wash—R. E. Divine, *Journ. Soc. Chem. Ind.*, **24**, 11, 1905.

[7] Chromium hydroxide is soluble in an excess of ammonia, forming a red solution. This can easily be shown by adding ammonia to a dilute solution of a chromium salt. No precipitate can be observed until the solution has been boiled a long time—W. Fischer and W. Herz, *Zeit. anorg. Chem.*, **31**, 352, 1902.

[8] Take care in the washing or the results may be 2 per cent. high when only one precipitation is made.

being projected from the crucible. After heating over the Bunsen flame, finish the ignition over the blast. Weigh as Cr_2O_3.

The following numbers were obtained with one precipitation, using the equivalent of 0·1034 grm. of Cr_2O_3, 2 c.c. of the tannin solution, 1 c.c. of sulphuric acid and 1 grm. of hydroxylamine hydrochloride:

| Cr_2O_3 found | . | . | 0·1033 | 0·1031 | 0·1034 | grm. |
| Error | . | . | − 0·10 | − 0·29 | 0·00 | per cent. |

Errors.—As a matter of fact, the results are generally high, and this has been attributed to the formation of chromium chromate,[1] $Cr_2O_3 . 3CrO_3$. Ignition of the hydroxide in hydrogen is said to give completely accurate results. Imperfect washing may also lead to the formation of alkali chromates from the alkalies in the reagents or solution.[2] Genth[3] recommends boiling the precipitate with sulphurous acid before it is weighed, in order to make sure that the chromates are reduced; Clouet[4] recommends boiling the precipitate with alcohol; and Clark[5] suggests removing the chromates by washing with dilute acetic acid and determining them by titration with Mohr's salt; the chromates may be also determined colorimetrically. With the method described above there is no need for any of these methods of purification.

Hence, two of the important errors in this determination arise from the solubility of the hydroxide in ammonia and the presence of alkalies in the calcined oxide.[6] If the excess of ammonia be expelled by prolonged boiling, the precipitate becomes slimy and difficult to wash, and so aggravates the second source of error.[7] The effect of a slight excess of ammonia need not be feared when hydroxylamine hydrochloride is used, because hydroxylamine, not free ammonia, will be present, and chromium hydroxide is not appreciably soluble in this menstruum. Again, the addition of tannin enables the precipitate to be more readily washed and thus facilitates the removal of alkalies.

It is interesting to note that the precipitated chromium hydroxide may be coloured either violet, green or intermediate tints. The green precipitate[8] is commonest with the alcohol reduction, the violet with the hydroxylamine reduction. The violet precipitate is nearly always obtained by the method described above. If tannin is present, the precipitate appears grey. The green precipitate seems to have a greater avidity for alkalies than the violet-coloured one and thus gives rather high results.

Effect of Phosphoric Acid.—When phosphoric acid is present, chromium phosphate will be precipitated.[9] In that case, fuse the ignited and weighed

[1] G. Rothang, *Zeit. anorg. Chem.*, **84**, 165, 1913; H. T. S. Britton, *Analyst*, **49**, 130, 1924.
[2] T. Wilm, *Ber.*, **12**, 2223, 1879; *Chem. News*, **41**, 222, 1880; F. P. Treadwell, *Ber.*, **15**, 1392, 1882. A. Souchay (*Zeit. anal. Chem.*, **4**, 66, 1865) thinks that the high results are due to the action of the ammonia on the glass vessels.
[3] F. A. Genth, *Amer. J. Science*, (3), **5**, 418, 1873.
[4] P. Clouet, *Ann. Chim. Phys.*, (4), **16**, 90, 1869.
[5] J. Clark, *Chem. News*, **24**, 304, 1871.
[6] For adsorbed sulphuric acid in the precipitated chromic hydroxide from solutions containing sulphuric acid, see H. E. Patten, *Amer. Chem. Journ.*, **18**, 608, 1896.
[7] J. Hanůs and J. Lukas (*Inter. Cong. App. Chem.*, 8, i, 209, 1912) quantitatively precipitate chromium from neutral or alkaline solutions—containing chromates, or chromic salts—by means of hydrazine hydrate or one of the derivatives of hydrazine—hydrazine sulphate, phenylhydrazine, thiosemicarbazide. The precipitation is more rapid and complete in the presence of ammonium chloride, and thiosemicarbazide gives best results. For hexamethylenetetramine as a precipitant, see P. Rây and A. K. Chattopadhya, *Zeit. anorg. Chem.*, **169**, 99, 1928; P. Rây, *Zeit. anal. Chem.*, **86**, 13, 1931. For mercury ammonium chloride, see W. Pumm, *Collegium*, 202, 1927.
[8] The violet hydroxide is possibly $Cr(OH)_3$; the green, $Cr_2O(OH)_4$.
[9] H. Baubigny, *Bull. Soc. chim.*, (2), **41**, 291, 1884; *Chem. News*, **50**, 18, 1884.

precipitate with sodium carbonate and a little sodium nitrite. Dissolve the melt in water acidified with nitric acid, and precipitate the phosphoric acid with ammonia and magnesia mixture. The chromium may be determined by difference, or precipitated from the filtrate as barium chromate, or determined volumetrically.

§ 262. The Volumetric Determination of Vanadium.

One method for the determination of vanadium is based on the reduction of vanadium pentoxide—V_2O_5—to vanadium tetroxide - V_2O_4—and the re-oxidation of the latter by a standard solution of potassium permanganate.[1]

Suppose we have to deal with the solution remaining after the colorimetric determination of chromium (page 526).[2] The boiling solution is reduced with sulphur dioxide from a syphon, and the excess of sulphur dioxide is expelled by passing a rapid current of carbon dioxide through the solution, which is then titrated at 70° 80° with a dilute solution of potassium permanganate approximately 0·01N, that is, 0·3161 grm. of $KMnO_4$ per litre[3] until a permanent pink colour is obtained. If the solution be titrated cold, the end-point is not so sharp.[4]

[1] W. F. Hillebrand, *Journ. Amer. Chem. Soc.*, **20**, 461, 1898; G. C. Kelley and J. B. Connant, *ib.*, **38**, 341, 1916; G. E. F. Lundell and H. B. Knowles, *ib.*, **43**, 1560, 1921; A. Bettendorff, *Pogg. Annalen*, **160**, 126, 1877; C. Czudnowicz, *ib.*, **120**, 17, 1863; C. Rammelsberg, *Ber.*, **1**, 158, 1868; B. W. Gerland, *ib.*, **10**, 1513, 1516, 1877; O. Manasse, *Liebig's Ann.*, **240**, 23, 1887; *Zeit. anal. Chem.*, **32**, 225, 1893; O. Lindemann, *ib.*, **18**, 99, 1879; G. Wegelin, *ib.*, **53**, 81, 1914; W. Hartmann, *ib.*, **66**, 16, 1925; J. Kassler, *ib.*, **77**, 290, 1929; F. A. Genth and G. von Rath, *Chem. News*, **53**, 218, 1886; **74**, 78, 1896; J. R. Cain, *Bull. Bur. Standards*, **7**, 377, 1911; E. de M. Campbell and C. E. Griffin, *Journ. Ind. Eng. Chem.*, **1**, 661, 1909; G. T. Dougherty, *ib.*, **7**, 419, 1915; D. J. Demorest, *ib.*, **4**, 249, 895, 1912; J. R. Cain and J. C. Hostetter, *ib.*, **4**, 250, 1912; J. R. Cain and D. J. Demorest, *ib.*, **4**, 256, 1912; R. B. Schaal, *ib.*, **13**, 698, 1921; G. L. Kelley and J. A. Wiley, *ib.*, **13**, 1053, 1921; G. Auchy, *ib.*, **1**, 455, 1909; G. Edgar, *Amer. J. Science*, (4), **25**, 332, 1908; F. A. Gooch and L. B. Stookay, *ib.*, (4), **14**, 369, 1902; F. A. Gooch and R. D. Gilbert, *ib.*, (4), **15**, 389, 1903; F. A. Genth, *ib.*, (3), **12**, 32, 1876; F. A. Gooch and G. Edgar, *ib.*, (4), **25**, 233, 1908; *Ber.*, **38**, 600, 1905; E. P. Alvarez, *Chem. Ztg.*, **33**, 149, 1909; P. Slawik, *ib.*, **36**, 171, 1912; A. Heinzelmann, *ib.*, **39**, 285, 1915; K. Swoboda, *ib.*, **52**, 1014, 1928; H. Mende, *ib.*, **53**, 178, 1929; K. Ries, *ib.*, **53**, 527, 1929; E. Färber, *ib.*, **55**, 691, 1931; E. Campagne, *Bull. Soc. chim.*, (3), **31**, 962, 1904; *Compt. rend.*, **137**, 570, 1903; A. Ditte, *ib.*, **101**, 698, 1885; C. Matignon and P. Monnet, *ib.*, **134**, 542, 1902; W. Heike, *Stahl Eisen*, **25**, 1357, 1905; H. König, *ib.*, **34**, 405, 1914; O. Wilms and P. Fischbach, *ib.*, **34**, 417, 1914; C. Hensen, *Kritische Untersuchung der Vanadin Bestimmungsmethoden*, Aachen, 36, 1909; P. Jannasch and H. E. Harwood, *Journ. prakt. Chem.*, (2), **97**, 93, 1918; T. Nakazono, *Journ. Chem. Soc. Japan*, **42**, 761, 1921; E. Müller and H. Just, *Zeit. anorg. Chem.*, **125**, 155, 1922; A. W. Hothersall, *Journ. Soc. Chem. Ind.*, **43**, 270, 1924; A. T. Etheridge, *Analyst*, **53**, 423, 1928; B. S. Evans and S. G. Clarke, *ib.*, **53**, 475, 1928; F. Ibbotson, *ib.*, **53**, 531, 1928; G. Scagliarini and P. Pratesi, *Atti. R. Accad. Lincei*, (6), **14**, 298, 1931; E. M. Utkina, *Zavodskaya Lab.*, No. 4, 17, 1933; C. H. Rich and G. C. Whittam, *Met. Chem. Eng.*, **13**, 238, 1915; E. C. Kraus, *ib.*, **16**, 418, 1917; F. L. Hamner, *ib.*, **17**, 206, 1917; R. Holverscheit, *Chem. Centr.*, (1), 977, 1890; F. T. Ressoul, *Ing. chim.*, **18**, 63, 1934; A. Travers, *Bull. Assoc. tech. Fonderie*, **8**, 383, 1934. H. E. Roscoe (*Journ. Chem. Soc.*, **11**, 928, 1871) considered the process by zinc reduction not reliable. For a comparison of gravimetric methods for the determination of vanadium, see L. Moser and O. Brandl, *Monats.*, **51**, 169, 1929.   J. E. Conley, *U.S. Bur. Mines Bull.*, **212**, vii, 239, 1923.

[2] If molybdenum and arsenic be present, the solution, after the determination of chromium (page 526), is acidified with sulphuric acid, and treated with hydrogen sulphide (page 276), when both arsenic and molybdenum together with traces of platinum from the crucible are precipitated. Boil the filtrate to expel hydrogen sulphide.

[3] 1 grm. $KMnO_4$ corresponds with 2·8776 grms. V_2O_4 for the oxidation $V_2O_4 \rightarrow V_2O_5$.

[4] The temperature of the solution is of importance; the best temperature is between 70° and 80°. If the titration be made at too low a temperature, the end-point is not sharp enough, and if at too high a temperature, the permanganate may be reduced by the hot sulphuric acid solution of manganous sulphate, as shown by A. C. Sarkar and J. M. Dutta (*Zeit. anorg. Chem.*, **67**, 225, 1910).

After the titration, again reduce the boiling solution with a current of sulphur dioxide, when $V_2O_2(SO_4)_3$ again passes to $V_2O_2(SO_4)_2$; or, generalised:

$$V_2O_5 + SO_2 = SO_3 + V_2O_4$$

Boil the solution while a rapid current of carbon dioxide is passing through until the escaping gas no longer decolorises a solution of potassium permanganate. Repeat the titration on the hot solution. The reduction and titration should be repeated once again. The last two results will probably be lower than the first and the mean of them represents the correct vanadium content of the given solution.[1]

If but a small quantity of permanganate be used, verify the presence of vanadium as follows:— Evaporate the solution to dryness in order to expel the sulphuric acid; take up the residue with 3–4 c.c. of water; acidify the solution with a few drops of nitric acid; and add two or three drops of hydrogen peroxide. A brownish-red colour indicates vanadium.

Hillebrand's Correction for Excess of Chromium.—If over about 0·005 grm. of chromium be present, a correction must be made, since in hot solutions chromic salts are oxidised by permanganate. Hence make a solution of potassium chromate containing the same amount of chromium as the solution under investigation. Reduce with sulphur dioxide as indicated for vanadium, and titrate at the same temperature with the standard permanganate. The amount of permanganate used must be subtracted from that taken in titrating for vanadium, and the difference represents that used in converting $V_2O_4 \rightarrow V_2O_5$. It is perhaps easier to determine the chromic and vanadic acids volumetrically by the following process than to apply these corrections.[2]

Volumetric Determination of Chromic and Vanadic Acids.—It might be added that processes have been devised for the simultaneous determination of these two compounds. Edgar's process[3] is based on the fact that hydrobromic acid will reduce vanadic acid to vanadium tetroxide $\cdot V_2O_5 \rightarrow V_2O_4$—and chromic acid to chromic oxide—$2CrO_3 \rightarrow Cr_2O_3$; and hydriodic acid will reduce vanadium tetroxide to the trioxide—$V_2O_4 \rightarrow V_2O_3$—and leave chromic oxide unaffected. The mixture of chromic and vanadic acids (about 0·2 grm.) is boiled in a flask (fig. 113) with 15 c.c. of hydrochloric acid and 2 grms. of potassium bromide. The flask is arranged so that a slow current of hydrogen from a Kipp's apparatus and wash-bottle passes while the solution is being boiled. The bromine vapour evolved owing to the reaction: $V_2O_5 + 2CrO_3 + 8HBr = V_2O_4 + Cr_2O_3 + 4H_2O + 4Br_2$, is led through a pair of Wölbling's flasks containing an alkaline solution of potassium iodide. When the reaction is over, the contents of the absorption bulbs are washed into an Erlenmeyer's flask; the solution is acidified with hydrochloric acid; and the free iodine, liberated by the action of the bromine on the potassium iodide—$Br_2 + 2KI = 2KBr + I_2$—is titrated with sodium thiosulphate in the usual way.

Two grams of potassium iodide, 15 c.c. of hydrochloric acid and 3 c.c. of syrupy phosphoric acid are now added to the solution in the boiling flask, and the distillation repeated as before in a current of hydrogen. The absorption

[1] According to Wegelin (*l.c.*) the method is accurate to within 0·2 per cent. when working on 0·3 to 0·4 grm. of the vanadium compound. The addition of manganous sulphate is helpful to accuracy should chlorine be present.

[2] For a method for determining the titration error in the presence of chromium, see I. Wada and R. Ishii, *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **19**, Nos. 394–7, 1932.

[3] G. Edgar, *Amer. J. Science*, (4), **26**, 333, 1908; R. Holverscheit, *Chem. Centr.*, (1), 977, 1890; C. Friedheim and H. Euler, *Ber.*, **28**, 2067, 1895; P. E. Browning, *Zeit. anorg. Chem.*, **13**, 113, 1897; *Amer. Journ. Sci.*, (4), **2**, 185, 1896; F. A. Gooch and R. W. Curtis, *ib.*, (4), **17**, 41, 1904; H. Ditz and F. Bardach, *Zeit. anorg. Chem.*, **93**, 97, 1915.

flasks are charged as before and the iodine liberated by the reaction—$V_2O_4 + 2HI = V_2O_3 + H_2O + I_2$—is absorbed by the alkaline potassium iodide and titrated as before. The second titration gives data for calculating the amount of vanadic acid in the original solution; and the first and second titrations give data for calculating the amount of chromic acid.
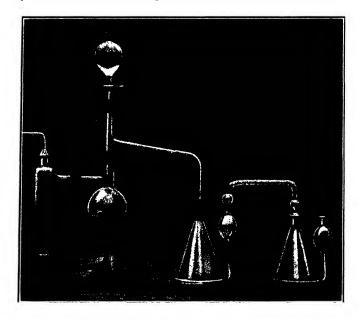
FIG. 113.—Simultaneous Determination of Chromic and Vanadic Acids.

A number of other methods have been developed which are all somewhat similar in principle.[1] The chromium and vanadium are converted to the state of chromate and vanadate by oxidisers such as sodium bismuthate, ceric sulphate, potassium bromate, perchloric acid or persulphates, with or without silver nitrate as catalyst. Persulphates are most commonly used. The excess of the oxidising agent is then removed by suitable means and the chromate and vanadate are reduced to chromium and vanadyl salts by titration with a standard solution of ferrous sulphate. The end-point is determined either potentiometrically or with an internal indicator. The volume of the standard ferrous sulphate solution used is a measure of the chromium and vanadium present. The vanadium in the reduced solution is again oxidised to the pentavalent state by titration with standard perman-

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[1] F. L. Hamner, *Met. Chem. Eng.*, **17**, 206, 1917; I. M. Kolthoff and O. Tomiček, *Rec. Trav. chim.*, **43**, 447, 1924; W. Brüggemann, *Chem. Ztg.*, **53**, 927, 947, 1929; R. Lang and F. Kurtz, *Zeit. anal. Chem.*, **86**, 288, 1931; W. Werz, *ib.*, **86**, 335, 1931; W. Hiltner and C. Marwan, *ib.*, **91**, 401, 1933; G. Thanheiser and P. Dickens, *Arch. Eisenhüttenw.*, **5**, 105, 1931–32; H. H. Willard and F. Fenwick, *Journ. Amer. Chem. Soc.*, **45**, 84, 1923; H. H. Willard and P. Young, *ib.*, **51**, 139, 149, 1929; *Ind. Eng. Chem.*, **20**, 764, 1928; *Ind. Eng. Chem. Anal. Ed.*, **4**, 187, 1932; *ib.*, **5**, 158, 1933; *ib.*, **6**, 48, 1934; D. J. Demorest, *Ind. Eng. Chem.*, **4**, 249, 1912; **5**, 895, 1913; G. L. Kelley and J. B. Connant, *ib.*, **8**, 719, 1916; G. L. Kelley, J. A. Wiley, R. T. Bohn and W. C. Wright, *ib.*, **13**, 939, 1921; I. M. Kolthoff and E. B. Sandell, *ib.*, *Anal. Ed.*, **2**, 140, 1930; H. H. Willard and R. C. Gibson, *ib.*, *Anal. Ed.*, **3**, 88, 1931; A. M. Duimov and O. A. Volodina, *Zavodskaya Lab.*, **2**, No. 9, 25, 1933.

ganate solution, as indicated on page 536. In this procedure a correction for chromium must be applied (page 537). Alternatively, the vanadium in the reduced solution is selectively oxidised to vanadate and, after destroying the excess of oxidiser, the solution is again titrated with standard ferrous sulphate solution. The volume of the latter used is a measure of the vanadium alone. The following is an adaptation of the procedure recommended by Willard and Young for determining chromium and vanadium in alloy steels. To the solution slightly acidified with sulphuric acid,[1] add 10 c.c. of 0·25 per cent. silver nitrate solution and about 2 grms. of ammonium persulphate. Boil for 10 to 15 minutes to oxidise the chromium and vanadium and destroy the excess of persulphate. Cool to room temperature, add 0·5 c.c. of 0·1 per cent. oxidised diphenylamine indicator[2] and titrate with 0·05N-ferrous sulphate solution.[3] At the end-point the colour changes sharply from purple to green. Now add to the reduced solution 0·1N-permanganate from a burette until an excess is just present. Then add three or four more drops and stand for 2 minutes to be sure that the colour persists and all the vanadium has been oxidised. Add 5 c.c. of 0·1M-sodium azide solution[4] to destroy the excess of permanganate and boil for 10 minutes in a fume cupboard to expel the hydrazoic acid. Cool to room temperature and titrate as before with ferrous sulphate.[5]

Volumetric Determination of Vanadium and Molybdenum.[6]— If a boiling solution of molybdic and vanadic acids be treated with sulphur dioxide, the vanadic acid, V_2O_5, is alone reduced to vanadium tetroxide, V_2O_4, provided the solution contains no more than 0·2 grm. of molybdic acid per 50 c.c. and approximately 1 c.c. of free sulphuric acid. When the reduction is complete, pass a current of carbon dioxide through the boiling liquid to drive off the sulphur dioxide. The vanadium tetroxide can be titrated in the usual way with 0·1N-potassium permanganate. Then pass the solution through a reductor containing amalgamated zinc and collect in 50–60 c.c. of a 10 per cent. solution of ferric alum; add 8-10 c.c. of syrupy phosphoric acid to decolorise the iron salt and titrate with 0·1N-potassium permanganate as before. The permanganate required for the latter titration includes that needed for con-

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[1] Chlorides, if present, must first be removed by precipitation with silver nitrate or by evaporating the solution to strong fumes with a slight excess of sulphuric acid.

[2] OXIDISED DIPHENYLAMINE INDICATOR.—Dissolve 0·32 grm. of barium diphenylamine sulphonate in water, add a slight excess of sodium sulphate solution, filter or decant and make up to 100 c.c. Put the volume of indicator solution needed for the particular titration in a small beaker, add 5 c.c. of water, 3 or 4 drops of concentrated sulphuric acid and 3 or 4 drops of 0·1N-potassium dichromate. Run in very dilute (0·01 to 0·02N) ferrous sulphate solution until a fraction of a drop just turns the purple colour to a bluish-green. The whole of this solution is then added to the solution under titration. A titration blank is eliminated by the use of this oxidised indicator—H. H. Willard and P. Young, *Ind. Eng. Chem. Anal. Ed.*, **5**, 154, 1933.

[3] Standardised against potassium dichromate with oxidised diphenylamine as indicator.

[4] Or 0·05N-sodium nitrite solution, drop by drop, until all the permanganate has been reduced, then add at once 1 grm. of urea to destroy the nitrous acid and boil for 5 minutes.

[5] Tungsten interferes and, if present, must be kept in solution as complex fluoride by the addition of hydrofluoric acid. Variant procedures are: (1) to reduce selectively the chromate by a measured excess of standard arsenite solution, the excess being determined by titration with permanganate. The vanadium is then determined by titration with ferrous sulphate—Kolthoff and Sandell (*l.c.*); (2) reduction of the chromate in acetic acid solution by hydrogen peroxide, followed by titration of the vanadate with ferrous sulphate. Sodium perborate is used as the source of hydrogen peroxide and the excess is destroyed by boiling —Willard and Fenwick (*l.c.*). For the simultaneous determination of chromium and vanadium by means of titanous chloride, see F. W. Atack, *Analyst*, **38**, 99, 1913.

[6] G. Edgar, *Amer. J. Science*, (4), **25**, 332, 1908; *Zeit. anorg. Chem.*, **58**, 375, 1908.

verting the V_2O_2 to V_2O_5, and for the conversion Mo_2O_3 to $2MoO_3$; the former is three times the amount consumed for the $V_2O_4 \rightarrow V_2O_5$ titration.[1]

Volumetric Determination of Vanadium and Iron.[2]—If a mixed solution of ferric and vanadic oxides, acidified with a little sulphuric acid, be treated in a similar manner, the first titration (after the sulphur dioxide reduction) corresponds with the conversion of V_2O_4 to V_2O_5, and of $2FeO \rightarrow Fe_2O_3$; and the second titration (after the zinc reduction) with $V_2O_2 \rightarrow V_2O_5$, and $2FeO \rightarrow Fe_2O_3$. Hence, with 0·1N-permanganate, the difference between the two titrations multiplied by 0·0045475 gives the amount of vanadic acid originally present, and the amount of iron can then be calculated from either titration.

Alternatively, after the first permanganate titration remove the excess of permanganate by boiling with a few c.c. of hydrogen peroxide. Cool. Add 8-10 c.c. of syrupy phosphoric acid to suppress the colour of the ferric iron and titrate the vanadium with standard ferrous sulphate solution as indicated on page 538.[3]

§ 263. The Gravimetric Separation of Chromium and Vanadium.

The gravimetric separation of chromium and vanadium is complicated by the fact that chromium salts or chromates in the presence of vanadium pentoxide may give chromium vanadate, $CrVO_4$, or a vanadato-chromate.

Instead of applying the colorimetric process for chromium, followed by the volumetric process for vanadium, these two constituents can be determined gravimetrically [4] in the following manner:—Hydrochloric acid, if present, is expelled from the solution by repeated evaporation with nitric acid. The solution is just neutralised with sodium hydroxide, acidified with acetic acid

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[1] For the determination of molybdenum and vanadium in admixture by means of titanous chloride, see A. Travers, *Compt. rend.*, **165**, 362, 1917; **166**, 289, 1918.

[2] G. Edgar, *Amer. J. Science*, (4), **26**, 79, 1908.

[3] R. G. Gustavson and C. M. Knudson (*Journ. Amer. Chem. Soc.*, **44**, 2756, 1922) give a method for the successive electrometric titration of iron, vanadium and uranium. For other methods for the determination of vanadium in the presence of iron, see C. W. Wright, *Chem. News*, **108**, 248, 1913; G. T. Dougherty, *Journ. Ind. Eng. Chem.*, **7**, 419, 1915; G. Hinard, *Ann. Chim. anal.*, (2), **2**, 297, 1920; K. Someya, *Zeit. anorg. Chem.*, **139**, 237, 1924; *Sci. Rep. Tohôku*, **14**, 577, 1925; J. Silberstein, *Chemist-Analyst*, **14**, 11, 1929; S. M. Gutman and N. V. Mikheeva, *Soobshch. Vsesoyuz Inst. Met.*, Nos. 5/6, 73, 1931; G. Thanheiser and P. Dickens, *Mitt. Kaiser Wilhelm Inst. Eisenf. Düsseldorf*, **13**, 187, 1931; P. L. Blankden, *Chem. Weekb.*, **29**, 263, 1932.

[4] The following is an alternative process for the separation of chromium and vanadium. The solution, after reduction with sulphurous acid, is nearly neutralised with a saturated solution of sodium carbonate. A slight excess of barium carbonate emulsion is added and the solution vigorously boiled for 10-15 minutes with further small additions of barium carbonate, provided not more than 2 grms. excess is present. Air should be excluded as much as possible. The precipitate is collected, washed with hot water, ignited and fused in a platinum crucible for 20 minutes with 2 grms. of sodium carbonate and 0·25 grm. of potassium nitrate. The cold cake is digested with water and filtered. The filtrate is treated with hydrogen peroxide to oxidise nitrites, boiled for 5-10 minutes, transferred to a separating funnel, vigorously shaken with a slight excess of nitric acid, just neutralised with sodium hydroxide and again acidified with an excess of 1 c.c. of nitric acid for each 100 c.c. of solution. An excess, say 20 c.c., of a 20 per cent. solution of lead nitrate is vigorously stirred in, when lead chromate alone is precipitated from the cold solution containing chromium, vanadium and uranium, according to A. A. Noyes, W. C. Bray and E. B. Spear (*Tech. Quart.*, **21**, 14, 1908; *Journ. Amer. Chem. Soc.*, **30**, 481, 1908; R. Cain, *Journ. Ind. Eng. Chem.*, **4**, 17, 1912). Only 0·0001-0·0003 grm. of chromium remains in solution, and no precipitate was obtained with solutions containing 0·1 grm. of vanadium. Lead vanadate is sparingly soluble and can be precipitated quantitatively in presence of a weaker acid—acetic acid and ammonium acetate. Lead uranate is precipitated from neutral or slightly alkaline solutions. If the filtrate is afterwards required, the lead is removed with hydrogen sulphide.

and a solution of lead acetate added to the boiling solution. Boil three or four minutes. The voluminous precipitate of lead chromate and lead vanadate [1] soon settles, provided too great an excess of lead acetate has not been added.[2]

Separation of the Chromium.—Evaporate the mixture to about 30 c.c. on a water bath. Add 2 grms. of solid potassium carbonate; evaporate to dryness; take up the residue with a little hot water; let the insoluble matter settle and decant the clear liquid through a filter-paper. Wash the filter-paper with water. If the insoluble residue is yellowish, wash any of it which may be on the paper back into the vessel containing the bulk of the residue and repeat the treatment with potassium carbonate. When a colourless residue [3] has been obtained, wash it well and evaporate the joint filtrates to about 15 c.c. Again treat this solution with potassium carbonate. The final filtrate contains the lead chromate. Acidify the solution with acetic acid —carbon dioxide is evolved, and lead chromate is precipitated. The solution is heated to boiling and lead acetate is added until all the chromium is precipitated. The precipitate is treated gravimetrically as indicated on page 335; or the lead chromate precipitate is collected on the asbestos mat in a Gooch crucible and then dissolved in hot hydrochloric acid (1 : 4). The solution is cooled, treated with an excess of ferrous sulphate, and titrated with standard dichromate or permanganate as directed on pages 180 and 501.

Precipitation of the Vanadium.—The precipitate of lead carbonate and lead vanadate [4] is dissolved in nitric acid, the solution evaporated to dryness and the residue taken up with dilute hydrochloric acid. The lead is precipitated as sulphide. Filter. Evaporate the solution down to a small volume and treat it with concentrated nitric acid, evaporate to dryness, transfer the residue to a platinum crucible and after calcination (fusion) weigh as V_2O_5. (For the effect of chlorides, see page 525.) The vanadium may here also be determined volumetrically (page 536) or colorimetrically.

Vanadium can also be determined by precipitation as ammonium vanadate.[5]

[1] T. Fischer, *Ueber die Bestimmung von Vanadinsäure*, Berlin, 1894; G. Sefström, *Pogg. Ann.*, **21**, 43, 1831; J. J. Berzelius, *ib.*, **22**, 1, 1831; H. E. Roscoe, *Liebig's Ann. Suppl.*, **8**, 95, 1872; E. Claassen, *Amer. Chem. Journ.*, **7**, 349, 1885/6; H. Cormimbœuf, *Ann. Chim. anal. app.*, **7**, 258, 1902; H. H. Barker and H. Schlundt, *Met. Chem. Eng.*, **14**, 18, 1916. H. F. Watts (*Western Chem. Met.*, **5**, 408, 1909; *Chem. News*, **101**, 34, 1910) precipitates lead vanadate in a solution just acid with nitric acid and containing 1 to 2 grms. of sodium acetate. The precipitate is dissolved in dilute nitric acid and the lead and nitric acid removed by evaporation with sulphuric acid. See E. Carrière and H. Guiter, *Compt. rend.*, **204**, 1339, 1937.

[2] For other methods of separation, see A. Carnot, *Compt. rend.*, **104**, 1850, 1887; M. E. Pozzi-Escot, *ib.*, **149**, 1131, 1909; V. von Klecki, *Zeit. anorg. Chem.*, **5**, 381, 1894; O. Lindemann, *Zeit. anal. Chem.*, **18**, 99, 1879; K. Roesch and W. Werz, *ib.*, **73**, 352, 1928; A. Jilek and V. Vicovský, *Coll. Czech. Chem. Comm.*, **4**, 1, 1932.

[3] The ether and hydrogen peroxide test for chromium can be made—G. Werther, *Journ. prakt. Chem.*, (1), **83**, 195, 1861. According to F. H. Storer, this reaction detects 1 part of potassium chromate in 40,000 parts of water. W. J. Karslake, *Journ. Amer. Chem. Soc.*, **31**, 250, 1909; C. Reichard, *Zeit. anal. Chem.*, **40**, 577, 1901; M. Martinon, *Bull. Soc. chim.*, (2), **45**, 862, 1886.

[4] R. Holverscheit, *Ueber die quantitative Bestimmung des Vanadins und die Trennung der Vanadinsäure von Phosphorsäure*, Berlin, 21, 1890.

[5] J. J. Berzelius, *Pogg. Ann.*, **22**, 54, 1831; K. von Hauer, *Journ. prakt. Chem.*, (1), **69**, 385, 1856; H. E. Roscoe, *Liebig's Ann. Suppl.* **8**, 101, 1872; W. Gibbs, *Proc. Amer. Acad.*, **10**, 242, 1875; *Amer. Chem. Journ.*, **5**, 371, 1883; A. Ditte, *Compt. rend.*, **104**, 982, 1887; A. Rosenheim, *Zeit. anorg. Chem.*, **32**, 181, 1902; F. A. Gooch and R. D. Gilbert, *ib.*, **32**, 174, 1902; *Amer. Journ. Sci.*, (4), **14**, 205, 1902; R. Holverscheit, *Ueber die quantitative Bestimmung des Vanadins und die Trennung der Vanadinsäure von Phosphorsäure*, Berlin, 11, 1890. For the use of cupferron in determining vanadium, especially in the presence of arsenic and phosphorus, see W. A. Turner, *Amer. Journ. Sci.*, (4), **41**, 339, 1916; *ib.*, (4), **42**, 109, 1916; L. Rolla and M. Nuti, *Giorn. Chim. ind. appl.*, **3**, 287, 1921; S. G. Clarke, *Analyst*, **52**, 466,

This is formed when a concentrated vanadate solution is treated with a saturated solution of ammonium chloride, or with solid ammonium chloride, followed by alcohol. The precipitate is washed with alcohol, dried, heated to expel ammonium chloride and afterwards heated with ammonium nitrate to constant weight. Roscoe and Holverscheit concluded that the solubility of the ammonium vanadate in the mother and wash liquors led to low results.

§ 264. The Colorimetric Determination of Vanadium.

In the absence of titanium, the hydrogen peroxide colorimetric process described for titanium can be applied, *mutatis mutandis*, to vanadium.[1] The reddish-brown colour is intensified by an excess of acid and partly bleached by an excess of hydrogen peroxide. The test is most exact when carried out in a solution containing 15–20 per cent. of sulphuric acid, 3 per cent. hydrogen peroxide being added, drop by drop, until the colour ceases to intensify. The prior addition of oxalic acid to the sulphuric acid solution is said to prevent bleaching by excess of hydrogen peroxide. Molybdenum and titanium interfere. The colour given by molybdenum is bleached by the addition of boric acid, which does not affect the vanadium coloration. The addition of hydrofluoric acid or ammonium fluoride has been recommended to suppress the colour given by titanium, if present. Any interference due to the presence of ferric salts and also titanium can be eliminated by phosphoric acid.

Mellor has developed a method for the simultaneous colorimetric determination of titanium and vanadium, based on the intensity of red rays in solutions of titanium and vanadium coloured with hydrogen peroxide and Fenton's acid.[2] Experience and visual acuity are necessary for accurate results. Gregory's colorimetric process [3] can be used for the colorimetric

1927; V. G. Rodeja, *Anales Soc. Espan. Fis. Quim.*, 12, 305, 379, 1915. For the separation of vanadium from arsenic, see C. Field and E. F. Smuts, *Journ. Amer. Chem. Soc.*, 18, 1051, 1896; from phosphorus, A. Kropf, *Chem. Ztg.*, 41, 877, 890, 1917; from chromium by 8-hydroxyquinoline, E. B. Sandell, *Ind. Eng. Chem. Ed.*, 8, 336, 1936; from iron, E. Deiss and H. Leysaht, *Chem. Ztg.*, 35, 869, 1911; P. Wenger and H. Vogelson, *Helv. Chim. Acta*, 2, 550, 1919; from molybdenum, J. Kassler, *Zeit. anal. Chem.*, 74, 276, 1928. For analyses of vanadinite and related minerals, see G. Surr, *Min. Eng. World*, 41, 203, 1914; for the assay of vanadic acid, G. Chesnau, *Ann. Chim. anal.*, 18, 108, 1913.

[1] V. von Klecki, *Zeit. anorg. Chem.*, 5, 374, 1894; L. Maillard, *Bull. Soc. chim.*, (3), 23, 422, 559, 1900; *Chem. News*, 82, 19, 1900; L. C. Barreswil, *Compt. rend.*, 16, 1085, 1843; A. Travers, *ib.*, 165, 362, 1917; 166, 289, 1918; G. Werther, *Journ. prakt. Chem.*, (1), 83, 195, 1861; C. Reichard, *Zeit. anal. Chem.*, 40, 577, 1901; 42, 95, 293, 1903; J. Meyer and A. Pawletta, *ib.*, 69, 15, 1926; J. Lukas and A. Jilek, *ib.*, 76, 348, 1929; J. Kassler, *ib.*, 77, 290, 1929; A. Kropf, *Zeit. angew. Chem.*, 35, 366, 1922; G. Misson, *Bull. Soc. chim. Belg.*, 31, 123, 1922; C. R. McCabe, *Journ. Ind. Eng. Chem.*, 5, 736, 1913; 6, 960, 1914; *Chem. News*, 104, 194, 202, 1911; S. G. Clarke, *Analyst*, 52, 527, 1927; B. S. Evans and S. G. Clarke, *ib.*, 53, 475, 1928; G. Fenner, *Chem. Ztg.*, 42, 403, 1918; T. Gedeon, *Magyar Chem. Fol.*, 37, 89, 1931; S. M. Gutman, *Soobshch. Vsesoyuz Inst. Met.*, 1, 66, 1931; P. Slawik, *Chem. Ztg.*, 34, 648, 1910; E. R. Wright and M. G. Mellon, *Ind. Eng. Chem. Anal. Ed.*, 9, 375, 1937. For the separation of vanadium from titanium, see W. R. Schoeller, *Analyst*, 61, 585, 1936.

[2] J. W. Mellor, *Trans. Cer. Soc.*, 12, 33, 1913. Dihydroxymaleic acid, $C_4H_4O_6 \cdot 2H_2O$— H. J. H. Fenton, *Journ. Chem. Soc.*, 9, 1064, 1908. See also P. Duez, *Bull. Assoc. tech. Fonderie*, 8, 570, 1934; S. Terrat, *Documentat. Sci.*, 4, 17, 1935; *Chem. Zentr.*, (1), 3819, 1935.

[3] A. W. Gregory, *Chem. News*, 100, 221, 1909; J. R. Cain and J. C. Hostetter, *Journ. Ind. Eng. Chem.*, 4, 250, 1912. The lower oxides of vanadium do not give the colour test. For other colour reactions, see L. Levy, *Compt. rend.*, 103, 1195, 1886; C. Matignon, *ib.*, 82, 1904; C. Reichard, *Chem. Ztg.*, 27, 1, 1903; V. von Klecki, *Zeit. anorg. Chem.*, 5, 374, 1894; C. Laar, *Ber.*, 15, 2086, 1882; G. Witz, *Dingler's Journ.*, 250, 271, 1883; G. Witz and F. Osmond, *Bull. Soc. chim.*, (2), 45, 309, 1886; R. Wagner, *Dingler's Journ.*, 223, 631, 1877; K. F. Mandelin, *Pharm. Zeit. Russland*, 22, 345, 361, 377, 1883; F. Kundrat, *Zeit. anal. Chem.*, 28, 709, 1889; *Chem. Ztg.*, 13, 265, 1889; M. Lucion, *Compt. rend.*, 103,

determination of vanadium in the presence of titanium. It is based on the orange coloration which is developed when an acid solution of vanadic sulphate is brought in contact with strychnine. The solution is at first coloured deep violet; this gradually changes to an intense orange. The intensity of the orange coloration depends upon the amount of vanadium in the solution. The process gives fairly satisfactory results in the presence of titanium, molybdenum and tungsten, but it is not satisfactory in the presence of iron. Of course the iron can be removed by fusion with sodium carbonate, and extraction with water. The use of concentrated sulphuric acid is a very unpleasant feature in this process.

It will be remembered that, if appreciable amounts of vanadium are present, the colorimetric process for titanium will be erroneous. The volumetric processes are not sensitive enough for the traces of vanadium usually found in British fireclays, unless relatively large quantities are taken for analysis.

§ 265. The Rapid Determination of Vanadium— Cain and Hostetter's Process.

The following volumetric method, due to Cain and Hostetter, enables a vanadium determination to be made in about half an hour. The process is based on the fact that vanadic acid can be quantitatively precipitated by ammonium phosphomolybdate, and the vanadium reduced to the quadrivalent condition by hydrogen peroxide without interference from the associated iron and molybdenum. The solution can then be titrated with permanganate in the usual way.

The solution under investigation in an Erlenmeyer's flask—containing possibly iron, titanium, chromium, vanadium, manganese—is heated to boiling and treated with ammonia; the precipitate is washed once or twice by decantation, and dissolved in nitric acid (sp. gr. 1·135). Boil the solution until it is free from fumes and oxidise it with potassium permanganate. Clear the solution by treatment with a slight excess of sodium sulphite solution, and boil the mixture until it is again free from nitrous fumes. Nearly neutralise the solution with ammonia and add an amount of a solution of sodium phosphate [1] equivalent to ten times as much phosphorus as there is vanadium present. Heat the solution to boiling and add sufficient ammonium molybdate (page 672) to precipitate all the phosphorus added as ammonium phosphomolybdate. Agitate the solution for about a minute. The precipitate, which settles rapidly, is washed three times by decantation with hot (80°) acid ammonium sulphate solution.[2] The washing liquid is filtered by suction through an asbestos-packed Gooch crucible. The last washing should be

1195, 1886; A. P. Vinogradov, *Compt. rend. Acad. Sci.* (*U.S.S.R.*), 249A., 1931; V. A. Silbermitz and L. V. Rozhkova, *Journ. Russ. Phys. Chem. Soc.*, **59**, 121, 1927; K. Bolchakov, *Tzvetnuie Metal*, 6, 487, 1931; M. B. Zapadinskii and V. M. Zhogina, *ib.*, 7, 513, 1932; D. Katakousinos, *Praktika*, 4, 448, 1931; *Chem. Zentr.*, (1), 845, 1932. For the colorimetric determination of vanadium with phosphotungstic acid, see A. P. Vinogradov, *Compt. rend. Acad. Sci.* (*U.S.S.R.*), 249A., 1931; E. B. Sandell, *Ind. Eng. Chem. Anal. Ed.*, 8, 336. 1936; H. H. Willard and P. Young, *Ind. Eng. Chem.*, 20, 765, 1928; E. R. Wright and M. G. Mellon, *ib.*, *Anal. Ed.*, 9, 251, 1937; W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, New York, 354, 1929; F. D. and C. T. Snell, *Colorimetric Methods of Analysis*, New York, 1, 373, 1936.

SODIUM PHOSPHATE SOLUTION.—Dissolve 124 grams of $Na_2HPO_4 . 12H_2O$ in a litre of water. 1 c.c. will precipitate 0·001 grm. of vanadium and it is equivalent to about 0·01 grm. of phosphorus. G. P. Baxter, *Amer. Chem. Journ.*, 28, 301, 1902.

ᵃ ACID AMMONIUM SULPHATE SOLUTION.—Mix 15 c.c. of aqueous ammonia (sp. gr. 0·9) with 1000 c.c. of water and 25 c.c. of sulphuric acid (sp. gr. 1·84).

decanted as completely as possible from the precipitate in the flask and the filter sucked dry. Change the filtration flask and draw hot concentrated sulphuric acid through the Gooch crucible by suction. This dissolves any of the precipitate on the filter. Transfer the sulphuric acid solution to the flask in which the precipitation was made. Wash the filtration flask with concentrated sulphuric acid. Every 0·01 grm. of phosphorus requires a final volume of 5 to 8 c.c. of the sulphuric acid. Heat the contents of the flask until the precipitate is all dissolved, add a few drops of nitric acid (1 : 25), and in two or three minutes, when sulphuric acid fumes are coming off vigorously, remove the flask from the hot plate. When cold, add 3 per cent. hydrogen peroxide solution, in small quantities at a time, with vigorous shaking after each addition, until the solution assumes a deep brown colour owing to the action of the peroxide on the molybdate. The brown coloration gives way to a clear green or blue.[1] Put the flask on the hot plate and, when the solution has been fuming four or five minutes, cool, add sufficient water to give an acidity 1 to 5 by volume,[2] and titrate at a temperature between 70° and 80°, as indicated in § 262, page 536.

§ 266. The Separation of Uranium.[3]

The filtrate from the silica, the pyrosulphate fusion or the hydrogen sulphide precipitation[4] is evaporated to about 100 c.c. and treated with an excess of ammonia,[5] ammonium carbonate and afterwards with ammonium sulphide.[6] The solution is stood overnight in a corked flask, filtered and the precipitate washed with water containing ammonium carbonate and sulphide in solution. The precipitate contains beryllium, titanium, zirconium and aluminium

[1] If the vanadium be not reduced, traces of nitric acid are probably present in the solution, since this acid oxidises quadrivalent vanadium. The nitric acid must be removed by the fuming process.

[2] If the solution has a greater acidity than 1 : 2, the end-point will be uncertain because of the deep yellow colour which quinquevalent vanadium imparts to concentrated sulphuric acid. A dilution of 1 : 5 gives a sharp end-point.

[3] See E. Einecke and J. Harms (*Zeit. anal. Chem.*, 99, 113, 1934) for a review of methods for determining uranium; also C. W. Davis, *U.S. Bur. Mines Bull.*, 212, vi, 199, 1923. M. F. Pisani, *Compt. rend.*, 52, 106, 1861; C. Friedel and E. Cumenge, *ib.*, 128, 532, 1899; *Amer. J. Science*, (4), 10, 135, 1900; G. Edgar, *ib.*, (4), 25, 332, 1908; (4), 26, 79, 1908; H. P. Foullon, *Jahrb. K. K. Geol. Reichsanst.*, 33, 23, 1887; C. Rammelsberg, *Chem. Centr.*, (3), 15, 806, 1884; C. Zimmermann, *Liebig's Ann.*, 213, 285, 1882; G. Alibigoff, *ib.*, 233, 117, 143, 1886; *Zeit. anal. Chem.*, 26, 632, 1887; H. Weber, *ib.*, 44, 420, 1905; A. Remelé, *ib.*, 4, 379, 1865; 26, 631, 1887; R. Fresenius and E. Hintz, *ib.*, 34, 437, 1895; A. Borntrager, *ib.*, 37, 436, 1898; C. Winkler, *ib.*, 8, 357, 1869; *Chem. News*, 43, 153, 1881; A. Guyard, *ib.*, 10, 13, 1864; A. C. Langmuir, *ib.*, 84, 224, 1901; *Journ. Amer. Chem. Soc.*, 22, 102, 1900; A. N. Finn, *ib.*, 28, 1443, 1906; *Chem. News*, 95, 17, 1907; O. P. Fritchle, *ib.*, 82, 258, 1900; *Eng. Min. Journ.*, 70, 548, 1900; W. Gibbs, *Zeit. anal. Chem.*, 12, 310, 1873; *Amer. J. Science*, (2), 39, 62, 1865; A. Patera, *Dingler's Journ.*, 180, 242, 1866; *Zeit. anal. Chem.*, 5, 228, 1866; W. Trautmann, *Zeit. angew. Chem.*, 24, 61, 1911; A. A. Blair, *Proc. Amer. Phil. Soc.*, 52, 201, 1913.

[4] Boiled to expel hydrogen sulphide, filtered to get rid of sulphur and oxidised with nitric acid. For the hydrogen sulphide precipitation, the acidity should correspond with about 1 c.c. of concentrated hydrochloric acid (sp. gr. 1·20), or 1 c.c. of concentrated nitric acid (sp. gr. 1·42), per 50 c.c. of the solution to get a clean separation from lead, cadmium and copper. If much more acid be present, some lead will remain in solution, as indicated on page 272.

[5] According to W. F. Hillebrand (*Bull. U.S. Geol. Sur.*, 78, 43, 1890), ammonia is necessary, otherwise the earths thrown down on neutralisation of the originally acid solution will be only partially redissolved.

[6] H. Rose, *Pogg. Ann.*, 96, 352, 1865; *Chem. News*, 7, 159, 1863; 8, 99, 1863; *Zeit. anal. Chem.*, 1, 410, 1862; W. Trautmann, *Zeit. angew. Chem.*, 24, 61, 1911; 25, 19, 1912. H. Boetticher (*Zeit. anal. Chem.*, 43, 99, 1904) deals with the separation of metals precipitated with ammonium sulphide. For the basic acetate separation, see H. Rheineck, *Chem. News*, 24, 233, 1871; A. Remelé, *Chem. News*, 10, 123, 158, 1864.

hydroxides [1] and the hydroxides of the rare earths, also cobalt, nickel, zinc, ferric and manganese sulphides, if present. If much alkalies, alkaline earths, iron or manganese be present, dissolve the precipitate in acid and repeat the precipitation. Collect the filtrates together. The filtrate contains all the uranium (possibly as uranyl ammonium carbonate), along with alkalies and possibly traces of the alkaline earths.

§ 267. The Gravimetric Determination of Uranium as Uranium Oxide.

Evaporate the filtrate containing the uranium to dryness in order to get rid of the greater part of the ammonium carbonate. Acidify the residue with hydrochloric acid and a few drops of nitric acid; boil to expel *all traces* of carbon dioxide; filter off the sulphur which separates; add ammonia, free from carbonate,[2] until the boiling solution is alkaline towards methyl red. A lemon-yellow voluminous precipitate of ammonium uranate—$(NH_4)_2U_2O_7 . nH_2O$—separates.[3] The precipitate rapidly becomes less bulky, darker in colour and more easy to filter and wash; but at best, it filters with difficulty.[4] Wash the precipitate with a 2 per cent. solution of ammonium nitrate.

When the precipitation is made with ammonia in the presence of alkalies or alkaline earths, the ammonium uranate is sure to be contaminated with these bases.[5] Hillebrand found that, on precipitation from hot solutions in the presence of ammonium chloride, the ammonium uranate was almost free from alkalies when the precipitation was carried out twice; and after three precipitations the uranate was practically pure.

The precipitate is ignited in a porcelain [6] or platinum crucible with the filter-paper, slowly at first so as to burn the paper, then for 15 minutes, or to constant

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[1] G. Lösekann (*Ber.*, **12**, 56, 1881) deals with the precipitation of aluminium and chromium by alkali sulphides. See L. Storch (*ib.*, **16**, 2014, 1885) for the precipitation of iron by alkali sulphides, and J. A. Norblad (*Bull. Soc. chim.*, (2), **23**, 64, 1875) for the separation of vanadium.

[2] It is essential that carbonates and organic matter be absent, as both prevent the precipitation of uranium. Organic matter, if present, can be destroyed by evaporation almost to dryness with an excess of concentrated sulphuric acid, prior to precipitation. Ammonium uranate is soluble in alkali carbonates and also slightly soluble in water; but it is not soluble in water containing ammonia, ammonium nitrate or ammonium chloride. The presence of tartaric acid, oxalic acid and many other non-volatile organic acids prevents the precipitation—R. Fresenius. If iron be separated from uranium by ammonium carbonate, the iron is free from uranium, but the uranium contains iron. The traces of iron can be removed from the precipitate of ammonium uranate by digestion with ammonium carbonate and filtration, when the uranium passes into the filtrate—G. L. Kelley, F. B. Meyers and C. B. Illingworth, *Journ. Ind. Eng. Chem.*, **11**, 316, 1919.

[3] When precipitated by sodium hydroxide, the precipitate, washed free from alkali, has the composition $2Na_2O.5UO_3$—J. Metzger and M. Heidelberger, *Journ. Amer. Chem. Soc.*, **31**, 1040, 1909. Ammonium sulphide may also be used in place of ammonia, but is said to give high results as, on ignition, partial oxidation to sulphate occurs—C. A. Pierlé, *Journ. Ind. Eng. Chem.*, **12**, 60, 1920. For precipitation by tannin, see R. N. Das-Gupta, *Journ. Indian. Chem. Soc.*, **6**, 763, 777, 1929; by ethylenediamine, J. A. Siemssen, *Zeit. anal. Chem.*, **52**, 773, 1913; by hydrogen peroxide, M. Wunder and P. Wenger, *Zeit. anal. Chem.*, **53**, 371, 1914; by 8-hydroxyquinoline, F. Hecht and W. Reich-Rohrwig, *Monats.*, **53** and **54**, 596, 1929; by pyridine, E. A. Ostroumov, *Ann. Chim. anal. Chim. appl.*, **19**, 89, 1937; *Zavodskaya Lab.*, **6**, 16, 1937.

[4] W. F. Hillebrand and G. E. F. Lundell (*Applied Inorganic Analysis*, New York, 369, 1929) recommend the addition of a macerated 7 cm. filter-paper after precipitation to assist in the filtration.

[5] R. Fresenius, *Quantitative Chemical Analysis*, London, **1**, 533, 1876; W. F. Hillebrand, *Amer. J. Science*, (4), **10**, 136, 1900.

[6] R. Schwarz (*Helv. Chim. Acta*, **3**, 330, 1920) says that if ignited in a platinum crucible, reducing gases tend to pass through the platinum and reduce the oxide. See also C. Zimmermann, *Liebig's Ann.*, **232**, 273, 1886.

weight, at a temperature not exceeding 900°.[1] Finally, let the precipitate cool slowly in a gradually decreasing flame. The crucible is kept in a slanting position to ensure a free circulation of air. The crucible is finally cooled in the desiccator, and the uranium weighed as the dark green or velvety black powder of the oxide—U_3O_8.[2] The filtrates contain lime, magnesia, alkalies and possibly some of the rare earths.

Separation of the Rare Earths and Calcium from Uranium.[3]—As mentioned above, if rare earths and calcium be present, some may be found with the precipitated ammonium uranate. In such cases the ammonia precipitate is dissolved in a slight excess of hydrochloric acid. The rare earths, also the bulk of the calcium, are now precipitated by adding a slight excess of a saturated solution of oxalic acid, followed by a little ammonium oxalate to reduce the amount of free mineral acid present, but excess must be avoided. The precipitate is filtered off and washed with 1 per cent. oxalic acid solution. The oxalate precipitate is converted to chloride and reprecipitated. The combined filtrates are evaporated to dryness and the oxalic acid destroyed by ignition. The residue is taken up in hydrofluoric acid, evaporated nearly to dryness and any rare earth fluorides which may separate are filtered off and washed with dilute hydrofluoric acid. The final filtrate is evaporated to dryness, the hydrofluoric acid fumed off with sulphuric acid, the residue taken up in nitric acid and the uranium precipitated with ammonium hydroxide. The rare earths and calcium can subsequently be separated by ammonium hydroxide.

§ 268. The Gravimetric Determination of Uranium as Uranium Phosphate.

Owing to the uncertainty in obtaining an oxide of constant composition when ammonium uranate is ignited, many prefer to precipitate the uranium as phosphate.[4] The old objection that the precipitate is too slimy to filter and wash readily does not apply if the precipitation be made as described below. Dissolve the oxide in dilute nitric acid.[5] Add ammonia until a precipitate just begins to form. Add just the right amount of nitric acid to clear the solution and then a tenfold excess of microcosmic salt, dissolved in a little water, together with 10 grms. of crystalline sodium thiosulphate.[6] The

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[1] According to A. Colani (*Ann. Chim. Phys.*, (8), 12, 59, 1907), the dissociation pressure of uranoso-uranic oxide, U_3O_8, is 157 mm. at 940°, and this is also the partial pressure of oxygen in the air. Thus appreciable dissociation will occur if the oxide be calcined at temperatures much higher than this. Compare R. Schwarz, *l.c.*

[2] This usually contains some patches of a yellowish-brown colour. As a check, Hillebrand and Lundell (*Applied Inorganic Analysis*, New York, 369, 1929) recommend determinations of the UO_2 and total uranium content of the precipitate, especially when the uranium was originally associated with elements which might escape complete separation.

[3] W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, New York, 467, 1929.

[4] C. Leconte, *Pharm. Journ.*, 13, 80, 1854; M. F. Pisani, *Chem. News*, 3, 211, 1861; *Compt. rend.*, 52, 72, 107, 1861; W. Knop and R. Arendt, *Chem. Centr.*, 737, 769, 803, 1856; E. F. Kern, *Journ. Amer. Chem. Soc.*, 23, 685, 1901; C. A. Pierlé, *Journ. Ind. Eng. Chem.*, 12, 60, 1920; R. Coomans, *Ing. chim.*, 10, 213, 1927. R. Schwarz (*Helv. Chim. Acta*, 3, 330, 1920) says that the separation of uranium as uranyl phosphate from alkali metals is impracticable owing to the fineness of the precipitate.

[5] Sulphuric acid is used if the precipitate is to be evaluated volumetrically, as described later.

[6] In the event of lime and magnesia being present, acidify the solution with acetic acid; add 5 c.c. of concentrated ammonium acetate to prevent the precipitation of calcium phosphate. Lime is determined in the filtrate by neutralising most, but not all, of the free acetic acid, and precipitation as oxalate and determination as sulphate (H. Brearley, *The Analytical Chemistry of Uranium*, London, 24, 1903). The magnesia is determined in the filtrate as usual.

solution becomes yellow and deposits a voluminous precipitate. Boil about 15 minutes. The precipitate then coagulates and settles rapidly. The precipitate is readily washed by decantation with water containing a little ammonium nitrate.[1] Transfer the precipitate to a Gooch crucible containing ignited asbestos, wash and dry. Ignite the precipitate at a red heat for 10 to 20 minutes.[2] If the precipitate be greenish coloured,[3] add a few drops of nitric acid (say, sp. gr. 1·42), dry over the flame and re-ignite at low redness over a Bunsen burner. The lemon-yellow compound $(UO_2)_2P_2O_7$ is formed on ignition. Multiply its weight by 0·7862 to get the equivalent amount of U_3O_8. The precipitate is somewhat hygroscopic and must not be needlessly exposed to the air before weighing.

In illustration of the results which can be obtained by precipitating uranium nitrate solutions, containing the equivalent of 0·1925 grm. of uranium, with microcosmic salt, Kern gives:

0·1921; 0·1927; 0·1925; 0·1905; 0·1903; 0·1921; 0·1918 grm.

§ 269. The Separation of Uranium as Uranium Ferrocyanide—Fresenius and Hintz's Process.

When phosphoric and arsenic acids are present, separation by the ordinary methods presents many difficulties and, in general, when members of the hydrogen sulphide group are present, the sulphide precipitate must be redissolved and reprecipitated a number of times to eliminate the uranium. Phosphoric acid too prevents clean separations of iron and uranium.

In this special case, Fresenius and Hintz [4] add an excess of potassium ferrocyanide to the slightly acid filtrate from the silica and saturate the liquid with sodium chloride to facilitate the flocculation of the precipitated uranium, copper and iron ferrocyanides. Otherwise the precipitate is exceedingly difficult to filter and wash. Wash the precipitate first by decantation and then on the filter-paper with a solution of sodium chloride. Digest the precipitate in the cold with dilute potassium hydroxide and, when the transformation of the ferrocyanides to hydroxides is complete, decant the liquid and wash the precipitate with water containing ammonium chloride and ammonia until ferrocyanide can no longer be detected in the acidulated filtrate. Dissolve the precipitate in hydrochloric acid [5] and, if necessary, concentrate the solution by evaporation. Neutralise the greater part of the acid with ammonia, add ammonium carbonate to the clear liquid, digest for some time in the cold, filter and wash the ferric hydroxide with water containing a little of the filtrate. Heat the filtrate to expel most of the ammonium carbonate, acidify with hydrochloric acid and boil the solution so as to dissolve the yellow flocculent precipitate. Remove copper from the solution by passing hydrogen sulphide through the hot liquid. The uranium can be determined in the filtrate as usual—page 545 or 546. See footnote 2, page 545, for the removal of traces of iron from uranium.

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[1] Test the filtrate for uranium with potassium ferrocyanide.

[2] The calcination of uranium phosphates in platinum crucibles leads to their rapid deterioration—A. Colani, *Ann. Chim. Phys.*, (8), **12**, 59, 1907.

[3] This is always the case if the ignition temperature be rather high. The green precipitate is generally supposed to be $U_2O_3 . P_2O_7$.

[4] R. Fresenius and E. Hintz, *Zeit. anal. Chem.*, **34**, 437, 1895; *Chem. News*, **72**, 206, 1895.

[5] If any ferrocyanide remains undissolved, repeat the treatment.

§ 270. The Separation of Vanadium and Uranium—Scott's Process.

This process is based on the fact that uranyl nitrate is readily soluble in glacial acetic acid, containing nitric acid in the proportion of 1 : 20, whereas vanadium pentoxide is insoluble in the same menstruum.[1] The mixed solution is evaporated to dryness with excess of nitric acid, or in the case of an ore, e.g. carnotite, 0·5 grm. is similarly evaporated with 40 c.c. of nitric acid (1 : 1). The residue is ignited and then boiled for 5 minutes with 25 c.c. of acetic-nitric acid mixture (20 : 1). After filtration, the filtrate is again evaporated to dryness, re-ignited and re-extracted with 15-20 c.c. of the acid mixture to remove the last traces of vanadium. The combined filtrates are evaporated to dryness, the residue dissolved in nitric acid (1 : 4) and heavy metals, other than uranium, precipitated by ammonia and ammonium carbonate in the cold. The filtrate is acidified with nitric acid, boiled to expel carbon dioxide and the uranium precipitated as ammonium uranate—page 545.

§ 271. Belohoubek's Volumetric Process for Uranium.

In 1867, Belohoubek[2] devised a method for the volumetric determination of uranium based on the reduction of uranic salts (UO_3) to uranous salts (UO_2) by means of zinc in acid solution, precisely in the same way that ferric salts are reduced, and, as with iron, subsequent titration with permanganate to re-oxidise the uranous salts. The reducing action is represented:

$$UO_2SO_4 + H_2 + H_2SO_4 = U(SO_4)_2 + 2H_2O$$

There is not a general agreement as to the accuracy of the results. Some consider that zinc reduces further than the UO_2 stage, and that the reduced solution must be exposed to the air to re-oxidise it to UO_2 before the perman-

[1] E. Péligot, *Ann. Chim. Phys.*, (3), **5**, 5, 1842; C. A. Pierlé, *Journ. Ind. Eng. Chem.*, **12**, 60, 1920; W. W. Scott, *ib.*, **14**, 531, 1922; *ib. Anal. Ed.*, **4**, 244, 1932. For the separation of vanadium and uranium by cupferron, see W. A. Turner, *Amer. Journ. Sci.*, (4), **42**, 109, 1916; for separations from titanium and zirconium, also by cupferron, A. Angeletti, *Ann. Chim. appl.*, **17**, 53, 1927; *Gazz. Chim. Ital.*, **51**, (1), 285, 1921. For the cupferron precipitation of uranous uranium, see V. Auger, *Compt. rend.*, **170**, 995, 1920; for the separation of uranium and beryllium, M. Wunder and P. Wenger, *Zeit. anal. Chem.*, **53**, 371, 1914; from thorium and rare earths, W. Riss, *Chem. Ztg.*, **47**, 765, 1923; from complex mixtures—W, Cr, Ni, Co, Fe and V, see H. König, *Chem. Ztg.*, **37**, 1106, 1913; from Zr, Ta, Cb, Ti, Fe, Mn, Pb, Sn, Cu, Ni and Cr—D. Guimaraes, *Ann. Acad. Brasil. Sci.*, **1**, 198, 1929.

[2] A. Belohoubek, *Journ. prakt. Chem.*, (1), **99**, 231, 1867; *Zeit. anal. Chem.*, **6**, 120, 1867; O. Follenius, *ib.*, **11**, 179, 1872; C. Zimmermann, *Liebig's Ann.*, **213**, 285, 1882; F. Ibbotson and S. G. Clarke, *Chem. News*, **103**, 146, 1911; E. de M. Campbell and C. E. Griffin, *Journ. Ind. Eng. Chem.*, **1**, 661, 1909; W. D. Engle, *Western Chem. Met.*, **4**, 450, 1908; A. A. Blair, *Proc. Amer. Phil. Soc.*, **52**, 201, 1913; V. Auger, *Compt. rend.*, **155**, 647, 1912; H. D. Newton and J. L. Hughes, *Journ. Amer. Chem. Soc.*, **37**, 1711, 1915; D. T. Ewing and E. F. Eldridge, *ib.*, **44**, 1484, 1922; N. H. Furman and I. C. Schoonover, *ib.*, **53**, 2561, 1931; D. T. Ewing and M. Wilson, *ib.*, **53**, 2105, 1931; I. M. Kolthoff and J. J. Lingane, *ib.*, **55**, 1871, 1933; G. E. F. Lundell and H. B. Knowles, *ib.*, **47**, 2637, 1925; M. A. Luyckx, *Bull. Soc. chim. Belg.*, **40**, 269, 1931; E. C. Hatt, *Zeit. phys. Chem.*, **92**, 513, 1918; T. Nakazono, *Journ. Chem. Soc. Japan*, **42**, 761, 1921; S. Kikuchi, *ib.*, **43**, 544, 1922; N. Kanô, *ib.*, **43**, 550, 1922; W. D. Treadwell and M. Blumenthal, *Helv. Chim. Acta*, **5**, 732, 1922; R. Schwarz, *ib.*, **3**, 330, 1920; K. Someya, *Zeit. anorg. Chem.*, **152**, 368, 1926; *Sci. Rep. Tôhoku Imp. Univ.*, **15**, 399, 1926; G. Scagliarini and P. Pratesi, *Ann. Chim. appl.*, **19**, 85, 1929; V. A. Matula, *Chem. Obzor.*, **6**, 124, 1931.

ganate titration is made.[1] Kern, however, states that the reduction does not proceed beyond the UO_2 stage when sulphuric acid is used, even upon five hours' boiling.[2]

The washed precipitate of, say, ammonium uranyl phosphate is dissolved in sulphuric acid, and the uranyl sulphate, UO_2SO_4, reduced with zinc, magnesium, copper or aluminium,[3] the amalgams of zinc, cadmium or bismuth, titanous sulphate or electrolytically, to uranous sulphate in an excess of sulphuric acid. According to Kern, the ratio of the volume of free sulphuric acid to the total volume of the solution should not be less than $1 : 5$, nor more than $1 : 6$. During the reduction, the colour of the solution passes from yellow to light green and finally to a green tinged with blue. This colour is retained even when the reduction has been in progress for four hours. Owing to the fact that there is no satisfactory test to determine whether all the uranyl sulphate has been reduced, it is best to let the reduction proceed for about an hour.[4] Dilute the solution with distilled water until it is almost colourless. Allow the solution to stand in contact with the air with occasional shaking and then titrate with N-potassium permanganate [5] until a permanent pink blush remains suffused through the solution. The oxidation by the permanganate is represented by the equation:

$$5U(SO_4)_2 + 2KMnO_4 + 2H_2O = 5UO_2SO_4 + 2MnSO_4 + 2KHSO_4 + H_2SO_4$$

In illustration of the results obtained with solutions of known strength, with zinc reduction, the following numbers might be quoted: [6]

Used	.	.	0·15406	0·15464	0·09643	0·19286	0·23050 grm.
Found	.	.	0·15400	0·15400	0·09625	0·19250	0·23100 grm.

[1] O. S. Pullman, *Amer. J. Science*, (4), **16**, 229, 1903; H. M. Goettsch, *Journ. Amer. Chem. Soc.*, **28**, 1541, 1906; H. N. McCoy and H. H. Bunzel, *ib.*, **31**, 367, 1909; W. D. Treadwell and M. Blumenthal, *l.c.*; N. H. Furman and I. C. Schoonover, *l.c.* If the solution be titrated electrometrically, any over-reduction is immaterial since the oxidation potential curve shows a break at the stage $U^{III} \rightarrow U^{IV}$ and a second break at the stage $U^{IV} \rightarrow U^{VI}$, hence the volume of the reagent added between the two breaks is a measure of the uranium present. If iron be present, a third and final break in the curve is given at the stage $Fe^{II} \rightarrow Fe^{III}$; thus iron and uranium can be determined simultaneously—D. T. Ewing and E. F. Eldridge, *l.c.*; D. T. Ewing and M. Wilson, *l.c.*; N. H. Furman and I. C. Schoonover, *l.c.* For other methods for determining uranium in the presence of iron, see S. Kikuchi, *Journ. Chem. Soc. Japan*, **43**, 544, 1922; V. A. Matula, *Chem. Obzor.*, **6**, 124, 1931; W. R. Bennett, *Journ. Amer. Chem. Soc.*, **56**, 277, 1934. On account of the possibility of over-reduction, both C. A. Pierlé (*Journ. Ind. Eng. Chem.*, **12**, 60, 1920) and R. Coomans (*Ing. chim.*, **10**, 213, 1927) condemn the volumetric process with permanganate.

[2] E. F. Kern, *Journ. Amer. Chem. Soc.*, **23**, 685, 1901; *Chem. News*, **84**, 224, 236, 250, 260, 271, 283, 1901; E. de M. Campbell and C. E. Griffin, *ib.*, **101**, 7, 1910; *Journ. Ind. Eng. Chem.*, **1**, 661, 1909.

[3] According to Kern (*l.c.*), the results with zinc, magnesium and aluminium are the same. Magnesium reduces fastest, zinc slowest. The reductor also gives satisfactory results. Kern did not get satisfactory results with stannous salts. Hydrochloric acid is also objectionable. Nitric acid must necessarily be absent.

[4] Kern says that 1 hour is sufficient for 0·1 grm. of uranium, 1½ hours for 0·2 grm. uranium.

[5] According to C. E. Griffin (*Min. Eng. World*, **37**, 247, 1912), permanganate solutions not exceeding 0·05N in strength give a sharper end-point than more concentrated solutions. W. R. Bennett (*Journ. Amer. Chem. Soc.*, **56**, 277, 1934) notes that the colour change of permanganate in coloured solutions is remarkably intensified by the addition of a little diphenylamine sulphonic acid.

[6] For interference of titanium, see V. Auger, *Compt. rend.*, **155**, 647, 1912; W. R. Bennett, *Journ. Amer. Chem. Soc.*, **56**, 277, 1934. If titanium be present, add a large excess of sodium tartrate and reduce with titanous chloride, using nitro-induline as indicator; then titrate the uranium with a ferric salt in acid solution, using potassium thiocyanate as indicator.

Volumetric Determination of Uranium and Vanadium.—Sulphur dioxide does not reduce uranyl solutions. Hence vanadium can be determined volumetrically in presence of uranyl salts. Griffin [1] tried to determine one in presence of the other by first reducing with sulphur dioxide and titrating with permanganate and then reducing both by zinc and titrating. By subtraction, the amount of permanganate required for the oxidation of each is found. Difficulties were encountered owing to the fact that, while zinc reduces the vanadic salts, V_2O_5, to vanadous salts, V_2O_3, the latter are nearly fully oxidised by air before one can titrate, no matter how rapidly the work is done. Reduction in the reductor, fig. 69, page 173, gave good results, but even then it is essential to keep an atmosphere of carbon dioxide above the liquid in the flask. The method is otherwise similar in principle to those indicated on pages 539 to 540 for vanadium and molybdenum, and for vanadium and iron.[2]

Evaluation of Commercial Salts.—Sodium uranate and uranium oxides, soluble in sulphuric acid, can be treated in a similar manner. There is a difficulty in dissolving the oxide U_3O_8. It dissolves very slowly in sulphuric acid. In that case, a little nitric acid, say 20 c.c. of concentrated acid, facilitates the dissolution. The solution must then be evaporated nearly to dryness to drive off the nitric acid, before the reduction and permanganate titration.[3]

Hillebrand [4] effects solution by heating, say, 0·2 grm. of the oxide in 10 to 15 c.c. of sulphuric acid (free from nitric acid), at 150° to 175°, in a sealed glass tube. The dry powder is placed in a thick glass tube, sealed at one end and the sulphuric acid (water 6, acid 1) [5] added through a long-stemmed thistle funnel, so as to keep the open end of the tube dry. When any carbon dioxide has had sufficient time to escape, draw out the open end in the blast blowpipe to a capillary point and seal off the tip. After digestion in a suitable furnace so that there is no risk if the tube bursts, let the tube cool, open by scratching the capillary end with a file and applying a hot glass rod. Wash the contents of the tube into a beaker, reduce with zinc and titrate with permanganate as described above.

In analyses of carnotite and uranium ores by different analysts, considerable variations—sometimes over 100 per cent.—appear in the amount of uranium. The ore does not contain a very large percentage of uranium and, if the amount falls below 2 per cent., the ore does not sell readily. Hence a small error may mean the difference between selling and not selling.[6] Commercial analyses of pitchblende to determine its value as an ore are usually stated in terms of

[1] C. E. Griffin, *Min. Eng. World*, **37**, 247, 1912.

[2] If uranium and vanadium occur together, A. N. Finn (*Journ. Amer. Chem. Soc.*, **28**, 1443, 1906) proceeds as follows:—The boiling solution is precipitated with an excess of sodium carbonate and the precipitate is dissolved in sulphuric acid and reprecipitated to eliminate traces of uranium. The combined filtrates, containing the uranium and vanadium, are heated to boiling and the uranium precipitated by adding 0·5 grm. of ammonium phosphate, followed by a slight excess of ammonia. Dissolve the washed precipitate in sulphuric acid and determine the uranium by the volumetric process (page 548). The filtrate is acidified with sulphuric acid and the vanadium determined volumetrically (page 536).

[3] For the rate of oxidation of uranous solutions, see H. N. McCoy and H. N. Bunzel, *Journ. Amer. Chem. Soc.*, **31**, 367, 1909.

[4] W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **78**, 90, 1889.

[5] With much stronger acid, Hillebrand obtained green crystals of a complex uranium salt in the sealed tube.

[6] W. F. Hillebrand and F. L. Ransome, *Amer. Journ. Sci.*, (4), **10**, 144, 1900; *Bull. U.S. Geol. Sur.*, **262**, 30, 1905; R. B. Moore and K. L. Kithil, *Bull. U.S. Bur. Mines*, **70**, 82, 1913.

$UO_2.2UO_3$, *i.e.* U_3O_8. This is an arbitrary assumption for the convenience of commerce.[1]

§ 272. Operations with Sealed Tubes.

Closing One End.—A piece of glass tubing—between 35 and 40 cm. long and 16-17 mm. internal diameter, with walls over 3 mm. thick—is carefully sealed at one end so that the glass is not thickened into a blob. If a blob does form, it can generally be removed by alternately heating and blowing. Tubes ready sealed at one end can be purchased from the dealers.

Charging the Tube.—The tube is washed (page 29) and dried. The dry powder under investigation is introduced into the tube so that the powder does not touch the side of the tube near the open end. The necessary acid is added by means of a long-stemmed funnel without wetting the sides of the tube near the open end.

Sealing the Tube.—About 5 cm. of the glass at the open end is very gradually heated by revolving it for several minutes in the smoky flame of a gas blowpipe. The tube is held inclined at an angle of about 45°. The blast is gradually turned on and the tube revolved until the glass begins to soften. One end of a glass rod, about 13 cm. long, is pressed against the edges of the glass tube—*a*, fig. 114. The blowpipe flame is reduced to about 8 or 10 cm. length, and directed at a point about 2 or 3 cm. away from the end to which the glass rod is attached. All the time the tube is being heated, it is slowly revolved so that the glass is heated as uniformly as possible, but not drawn
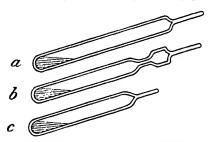
FIG. 114.—Three Stages in Sealing the Tube.

out.[2] The glass begins to thicken and the inside diameter of the tube contracts (see the photograph, fig. 115). When the inside diameter of this part of the tube has contracted to about 3 mm., the tube is withdrawn from the flame and the thickened portion is drawn out to form a capillary end—*b*, fig. 114. In a few seconds, when the capillary has cooled until it is rigid, seal the tip as shown at *c*, fig. 114. The tube is allowed to cool, capillary end upwards.

Heating the Sealed Tube.—The sealed tube is then placed in a metal cylinder with a screw cap. The metal cylinder is placed in a cold tube furnace—Meyer's, Gattermann's, Volhard's, Habermann's.[3] The tube furnace is gradually heated to the desired temperature. The furnace is placed so that no damage will be done if the tube bursts. The gas is extinguished when the tube has been heated long enough and the tube allowed to cool.

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[1] For a colorimetric process for uranium, based upon the yellow colour produced by potassium ferrocyanide in the presence of uranium salts, see A. Bruttini, *Gazz. Chim. Ital.*, **3**, 251, 1893; M. Tissier and H. Bénard, *Compt. rend. Soc. biol.*, **99**, 1144, 1928; J. Tschernichov and E. Guldina, *Zeit. anal. Chem.*, **96**, 257, 1934. The coloration is perceptible with 0·00001 grm. of uranium in 1 c.c. For the use of salicylic and gallic acids in the colorimetric determination of uranium, see A. Müller, *Chem. Ztg.*, **43**, 739, 1919, and R. N. Das-Gupta, *Journ. Indian Chem. Soc.*, **6**, 763, 777, 1929, respectively; for quinaldinic acid, P. Ráy and M. K. Bose, *Zeit. anal. Chem.*, **95**, 400, 1933.

[2] Hard glass tubes are not usually thickened, but drawn out at once into a wide capillary about 1¼ cm. long. The flame is directed at the base of this capillary, and the glass gradually drawn out so as to form a capillary 2 or 3 cm. long. This is sealed off at the tip. An oxy-coal gas flame gives the best results with hard glass.

[3] L. Meyer, *Ber.*, **14**, 1087, 1883; J. Volhard, *Liebig's Ann.*, **284**, 233, 1895; J. Habermann, *Zeit. anal. Chem.*, **13**, 165, 1874.

Opening the Sealed Tube.—When *quite* cold, withdraw the tube from the iron casing so that the capillary end, and only the capillary end, projects. If the reaction in the tube is such as to develop gas, place the tip of the capillary in the Bunsen flame so as to drive out any liquid which has condensed there.
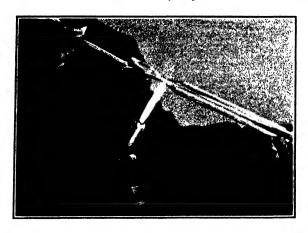
FIG. 115.—Sealing the Glass Tube.

Then heat the tip until the glass softens. The pressure inside the tube blows a vent-hole in the glass. When the pressure is relieved, and *not before*, withdraw the tube from its metal casing, file a mark on the glass tube about 2 cm. below the base of the capillary and touch the file mark with the red-hot tip of a drawn-out piece of glass tubing. The tube will crack, and the crack is carried round the tube by means of the hot glass tip. The end of the tube is then removed. The tube is kept as nearly horizontal as possible during this operation, so as to prevent fragments of glass dropping into the tube. The contents of the tube are then washed into a beaker and treated as required.

CHAPTER XXXV.

ZIRCONIUM, THORIUM AND THE RARE EARTHS.

§ 273. The Detection and Separation of Zirconium.

Minute quantities of zirconium occur in many if not most silicates of the type of Cornish stone.[1] Zirconia is also used as a constituent of certain white enamels and opaque glazes, and in special cases as a high temperature refractory material. In the regular course of a silicate analysis, zirconia appears with the ammonia or ammonium sulphide precipitate and, if ignored, would be reported as alumina. If the zirconia is to be determined, its weight must be deducted from the weight of the alumina as determined by the method of pages 164 and 198.

The presence of zirconia in a silicate or other material must first be established by qualitative test, otherwise any gravimetric procedure may be a sheer waste of time.

Tests for Zirconium. (1) *Biltz and Mecklenburg's Test.*[2]—Fuse a small quantity of the substance, free from phosphates, with sodium carbonate on a loop of platinum wire in an oxidising flame. When the action is complete, cool and decompose the bead by digestion with 10 per cent. (by volume) sulphuric acid. Just bring to the boil and filter off any undecomposed material or silicic acid which may separate out at this stage. Cool, add a moderate excess of pure hydrogen peroxide to peroxidise titanium, if present, followed by a generous excess of disodium phosphate. A gelatinous precipitate shows the presence of zirconium.[3] Iron, aluminium, the rare earths, thorium, beryllium and peroxidised titanium do not interfere, but tin must be absent.

(2) *Bellucci and Savola's Test.*[4]—In applying this test hydrochloric acid alone must be present. Hence to the acid solution (other than hydrochloric acid) add an excess of ammonia, filter and wash. Dissolve the precipitate in warm hydrochloric acid (1 in 3) and to the solution add an equal volume of a 1 per cent. solution of β-nitroso-α-naphthol in 95 per cent. alcohol. The presence of zirconium is shown by a red coloration. Aluminium, titanium, thorium, cerium and lanthanum salts give no colour, but iron should be absent. The limit of the test is 0·05 mgrm. ZrO_2 per c.c.

(3) *de Boer's Test.*[5]—Alizarin sulphonic acid gives a violet colour with zirconium, aluminium, yttrium, cerium, erbium, thallium, columbium,

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[1] For the rarer constituents of clays, including zirconia, see A. Fioletov, *Keram. Rundsch.*, **35**, 270, 1927; **37**, 659, 1929.

[2] W. Biltz and W. Mecklenburg, *Zeit. angew. Chem.*, **25**, 2110, 1912.

[3] A gradual separation of silicic acid from the solution on standing must not be mistaken for zirconium phosphate.

[4] I. Bellucci and G. Savola, *Atti 1. Congr. naz. Chim. pur. appl.*, 483, 1923; *Chem. Zentr.*, (1), 2531, 1924.

[5] J. H. de Boer, *Chem. Weekb.*, **21**, 404, 1924; *Rec. Trav. chim.*, **44**, 1071, 1925.

tungsten, titanium, thorium, molybdenum and uranium, but all colour reactions disappear, except that with zirconium, if concentrated hydrochloric acid be added. Fluorides must be absent, since even traces turn the reddish-violet colour, given by zirconium, to yellow.

(4) *Feigl's Test*.[1]—Hydrogen peroxide is first added to the hydrochloric acid solution of the material under test, to inhibit the interference of titanium, molybdenum and tungsten, if present. A drop of the solution is then placed on a filter-paper which has been impregnated in a solution of 0·1 grm. of *p*-dimethylaminoazophenylarsinic acid in 5 c.c. of concentrated hydrochloric acid and 100 c.c. of alcohol. The paper is then immersed for a short time in 2N-hydrochloric acid at 50°–60°, to dissolve the excess of reagent from it. A brown spot, insoluble in the acid, indicates zirconium. The sensitivity is of the order of 1 in 500,000. Very few substances are said to interfere seriously with the test. The brown stain, given by stannic salts, does not result if the concentration of the acid be increased.[2]

§ 274. The Gravimetric Determination of Zirconium as Phosphate.[3]

As indicated above, in a normal silicate analysis zirconia, if present, will appear in the ammonia precipitate and will be weighed with the other mixed oxides. Subsequently, on fusion with pyrosulphate, it will pass into the stock solution as sulphate. Hence, after the colorimetric determination of iron and titanium (pages 185, 189), the remainder or an aliquot part of the stock solution, depending on the amount of zirconia present, is taken and any platinum, which may have passed into solution by the action of the pyro-sulphate on the walls of the crucible, is precipitated by saturating the liquid with hydrogen sulphide at 40°–50°.[4] After filtration and washing, the excess of hydrogen sulphide is removed by passing a current of hydrogen through the warm liquid. An excess of pure hydrogen peroxide is added to peroxidise any titanium in the solution; it is essential that an excess be always present during the subsequent precipitation of the zirconium, otherwise titanium phosphate will be precipitated. Sufficient concentrated sulphuric acid (sp. gr. 1·84) is now added so as to bring the total amount of free sulphuric acid in the solution up to about 11 per cent. by volume—that is approximately

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[1] F. Feigl, P. Krumholtz and E. Rajmann, *Mikrochem.*, 9, 395, 1931.

[2] It must be borne in mind that most, if not all, of the above tests will probably be given by hafnium—*e.g.* the phosphate test—hence they do not serve to discriminate between zirconium and hafnium. For other tests for zirconium, see F. Pavelka, *Mikrochem.*, 4, 199, 1926; 8, 345, 1930.

[3] G. Steiger, *Journ. Wash. Acad. Sci.*, 8, 637, 1918; P. Nicolardot and A. Réglade, *Compt. rend.*, 168, 348, 1919; G. E. F. Lundell and H. B. Knowles, *Journ. Amer. Chem. Soc.*, 41, 1801, 1919; 42, 1439, 1920; J. Brown and H. T. Madden, *ib.*, 42, 36, 1920; G. Hevesy and K. Kimura, *ib.*, 47, 2540, 1925; J. H. de Boer, *Zeit. anorg. Chem.*, 144, 190, 1925; O. Ruff and E. Stephan, *ib.*, 185, 217, 1929; W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, New York, 446, 1929; H. F. Harwood, *Tids. Kjemi Berg.*, 12, 23, 1932; T. R. Cunningham and R. J. Price, *Ind. Eng. Chem. Anal. Ed.*, 5, 334, 1933; S. G. Simpson and W. C. Schumb, *ib.*, 5, 40, 211, 1933; M. Wunder and B. Jeanneret, *Zeit. anal. Chem.*, 50, 733, 1911; J. D. Ferguson, *Eng. Min. Journ.*, 106, 356, 1918; United Steel Co. Ltd., *Standard Methods of Analysis*, Sheffield, 54, 1936. For reviews of the methods of determining zirconium, see M. Frommes, *Zeit. anal. Chem.*, 96, 288, 1934; E. Einecke and J. Harms, *ib.*, 99, 113, 1934; J. W. Marden, *U.S. Bur. Mines Bull.*, 212, viii, 281, 1923.

[4] If the solution be boiled, zirconium and titanium may be precipitated by hydrolysis of their salts, especially if the amount of free sulphuric acid is low.

20 per cent. by weight.[1] 1 to 2 grms. of monohydrogen ammonium phosphate, $(NH_4)_2HPO_4$, are added[2] and the solution digested for 2 hours at 40°–50°. If only traces of a precipitate have then formed, cool and stand overnight, but if the amount is appreciable, add the pulp of a 9 cm. filter-paper, allow to settle and then filter. Wash the precipitate with a cold 5 per cent. solution of ammonium nitrate until it is free from sulphate.[3] Transfer the filter-paper to a weighed crucible, dry and then char the paper at a low temperature. Finally, partially cover the crucible and burn off the carbon very carefully, as the precipitate shows a marked tendency to spurt. Ignite over a Méker burner, cool and weigh as ZrP_2O_7. Multiply the weight by 0·4645 to obtain the corresponding weight of zirconium oxide, ZrO_2. Owing to the hydrolysis of the precipitate on washing (see footnote 3), the ignited precipitate will not exactly correspond in composition to ZrP_2O_7, but where small amounts of zirconia are involved the error is negligible. However, when great accuracy is essential, or when the amount of zirconia is large, as in the analysis of zircon or crude zirconium oxide, the following procedure should be adopted. The ignited residue is fused for some considerable time with about ten times its weight of sodium carbonate. The cold cake is digested with water until decomposed, the residue filtered off, washed with a 2 per cent. solution of sodium carbonate and finally with water. Since zirconium phosphate is not readily decomposed by sodium carbonate, unless a generous excess of the latter has been taken and the fusion prolonged, it may be necessary at this stage again to fuse with sodium carbonate and extract as before in order to eliminate the last traces of phosphorus pentoxide. The washed residue is ignited, fused with pyrosulphate and the cold cake taken up in dilute sulphuric acid. After removal of platinum from the solution, as indicated above, the zirconium is precipitated from the hot solution by ammonium hydroxide and washed with a hot 2 per cent. solution of ammonium nitrate.[4] As usual, the precipitate is redissolved and reprecipitated to free it from alkali salts. After ignition, the residue is ignited and weighed as ZrO_2.

The Determination of Hafnium.—Any hafnium present will be precipitated with the zirconium and reported as zirconium oxide. Since hafnium normally accompanies zirconium, the residue of nominal zirconium oxide may contain from traces up to appreciable quantities of hafnium, depending on the nature of the material under analysis and on its source. The approximate content of hafnium, if and when required, can be calculated from the ratio of the weights

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[1] When practicable, the total volume of the solution should be adjusted to the amount of zirconium present. Hillebrand and Lundell (*l.c.*) recommend a volume of 25 c.c. for 0·5 mgrm. of zirconium to 200 c.c. for 0·1 grm., but with materials of unknown zirconia content no general rule can be laid down.

[2] Hillebrand and Lundell (*l.c.*) say that a 10- to 100-fold excess of phosphate should be taken over that needed to form $Zr(HPO_4)_2$, and that the smaller the amount of zirconia the larger should be the excess. The remark under footnote 1 again applies. V. A. Oshman and T. K. Zerchaninova (*Redkie Metal*, **3**, 36, 1934) say that, when the amount of zirconia is small, the amount of free sulphuric acid should not exceed 1 per cent., otherwise there will be loss of zirconia.

[3] The precipitate tends to hydrolyse on washing and consequently the volume of wash liquor should be kept at a minimum. Owing to hydrolysis, the washings will never be completely free from phosphate, but the disappearance of sulphate from them will indicate when the washing is nearing completion.

[4] If thorium is present, the precipitated hydroxide is redissolved in sulphuric acid, and the precipitation as phosphate repeated in order to remove traces of thorium. Columbium and tantalum are also precipitated in part and it is advisable to remove them first. A cleaner separation of zirconium from cerium results if the latter is in the trivalent state—Hillebrand and Lundell (*l.c.*).

of the mixed oxides to that of the mixed phosphates [1] *on the assumption that the hydrolysis of the phosphates on washing has not caused their composition to deviate sensibly from ZrP_2O_7 and HfP_2O_7 respectively.* If, for example, the weight of the mixed oxides be w_1 and that of the mixed phosphates be w_2, then $a + b = w_1$ and $2 \cdot 1528a + 1 \cdot 6744b = w_2$, where a and b are the respective weights of zirconium and hafnium oxides. It must be borne in mind that this procedure involves (1) an assumption which is not proven, and (2) the error inherent in all indirect processes (see pages 221 *et seq.*).

§ 275. Gravimetric Determination by "Cupferron."

In acid solution, cupferron quantitatively precipitates iron, titanium and zirconium with varying amounts of thorium, cerium and the other rare earths, while aluminium, beryllium, manganese, uranium and the remainder of the rare earths pass into solution.[2] On ignition, the metals present in the cupferron complex are wholly converted into oxides; thus in this process there is no complication due to the uncertainty in the conversion factor as in the phosphate precipitation. The procedure of Lundell and Knowles, adapted to the normal course of a silicate analysis, is as follows: An aliquot portion of the stock solution from the pyrosulphate fusion of the mixed oxides is taken and the hydroxides precipitated by ammonia. After filtration and washing, dissolve the precipitate in dilute sulphuric acid. Alkali salts, which tend to be carried down by the cupferron precipitate, are hereby removed. Just neutralise the solution with ammonia and then redissolve the precipitate in sufficient sulphuric acid to give an excess of about 1 per cent. by volume. Saturate the solution with hydrogen sulphide, filter off and wash any platinum which is precipitated. To the filtrate and washings add an amount of tartaric acid equal to five times the weight of mixed oxides in solution.[3] Add excess of ammonia to the solution and again saturate it with hydrogen sulphide. Filter off the precipitated ferrous sulphide and wash it with a dilute solution of ammonium chloride containing a little colourless ammonium sulphide. Sulphuric acid is added to the filtrate and washings until they contain about 10 per cent. by volume of free acid. Boil to expel hydrogen sulphide and then cool to 10°. A 6 per cent. aqueous solution of cupferron is added until the initial curdy precipitate is followed by a fine white one which redissolves, thus showing that excess of the precipitant is present. Digest for 5 minutes, filter and wash the precipitate thoroughly with cold 10 per cent. (by volume) hydrochloric acid. Dry and carefully char the paper in a weighed platinum crucible, then burn off the carbon and ignite over a Méker burner. Cool and weigh as mixed oxides of zirconium and titanium. From the weight of mixed oxides subtract the proportionate amount of titanium oxide, as previously found in the colorimetric determination of titanium. If rare earth oxides are also present, fuse up the residue of mixed oxides in the platinum crucible with pyrosulphate. Cool, extract the cake and dissolve it in 10 per cent.

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[1] G. Hevesy and K. Kimura, *Journ. Amer. Chem. Soc.*, **47**, 2540, 1925; W. R. Schoeller, *Analyst*, **52**, 736, 1927.

[2] W. M. Thornton, junr., and E. M. Hayden, junr., *Amer. Journ. Sci.*, (4), **38**, 137, 1914; J. Brown, *Journ. Amer. Chem. Soc.*, **39**, 2358, 1917; G. E. F. Lundell and H. B. Knowles, *ib.*, **42**, 1439, 1920; *Journ. Ind. Eng. Chem.*, **12**, 562, 1920; O. Baudisch and V. L. King, *ib.*, **3**, 629, 1911; A. Angeletti, *Gazz. Chim. Ital.*, **51**, (1), 285, 1921.

[3] This weight is known from the total weight of the ammonia precipitate and from the volume of the stock solution taken for the determination.

sulphuric acid.[1] Precipitate the rare earths in the solution by hydrofluoric acid (page 563), followed by a second precipitation as oxalates (page 567). The zirconium oxide is determined by difference.

§ 276. Gravimetric Determination of Zirconium as Arsenate, Phenylarsinate or Selenite.

1. *Precipitation as Arsenate.*—In nitric acid solution zirconium (with hafnium) is precipitated by disodium hydrogen arsenate as zirconyl hydrogen arsenate, $ZrOHAsO_4$.[2] The precipitate is dissolved in sulphuric acid and hydrazine and hydrochloric acid are added. The arsenic is distilled off as chloride, followed by a double precipitation of zirconium by ammonia from the residual solution. The interference of titanium and ceric cerium is prevented by respective oxidation and reduction with hydrogen peroxide prior to the precipitation of the zirconium. If thorium is present the precipitation must be made from a solution which is approximately 1·13N in nitric acid. This method has not been extensively used.

2. *Precipitation by Phenylarsinic Acid.*—Zirconium is said to be quantitatively separated from all metals except hafnium and tin in 10 per cent. hydrochloric or sulphuric acid solution by phenylarsinic acid.[3] Double precipitation is necessary to effect complete separation from thorium, uranium, phosphates and large amounts of iron. Titanium, when present, is kept in solution by hydrogen peroxide. A 10 per cent. aqueous solution of the reagent is used in ten- to twenty-fold excess. The precipitation is made in boiling solution and the precipitated zirconium phenylarsinate washed with 1 per cent. hydrochloric acid, dried, ignited and weighed as ZrO_2.

If further work confirms the original investigations, phenylarsinic acid promises to be a most valuable reagent for the determination of zirconia in virtue of its selectivity, the absence of a conversion factor and from the fact that it permits of a separation of zirconium from phosphorus (see below).

Separation from Phosphorus.—When phosphates are present, the concentration of sulphuric acid is kept so high (about 40 per cent. by weight) that the zirconium phosphate remains dissolved. An excess of phenylarsinic acid is added and the solution diluted down to about 10 per cent. by weight of sulphuric acid. The precipitate is dissolved in sulphuric acid (1 in 1) and a second precipitation made as in the first instance.[4]

3. *Precipitation as Basic Selenite.*—An aqueous solution of selenious acid

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[1] If desired, the solution can be made up to, say, 100 c.c., and the titanium in 50 c.c. determined either colorimetrically or volumetrically, according to the amount present. The remainder of the solution is used for the determination of the rare earth oxides.

[2] L. Moser and R. Lessnig, *Monats.*, 45, 323, 1924; *Zeit. anal. Chem.*, 68, 468, 1926; K. Schröder, *ib.*, 68, 233, 1926; W. C. Schumb and E. J. Nolan, *Ind. Eng. Chem. Anal. Ed.*, 9, 371, 1937. Compare S. R. Paijkull, *Bull. Soc. chim.*, (2), 20, 65, 1873; *Öfvers. Acad. Förh. Stockholm*, 30, No. 6, 21, 1873.

[3] A. C. Rice, H. C. Fogg and C. James, *Journ. Amer. Chem. Soc.*, 48, 895, 1926; F. W. Arnold, junr., and G. C. Chandlee, *ib.*, 57, 8, 1935; P. Klinger and O. Schliessmann, *Arch. Eisenhüttenw.*, 7, 113, 1933; P. Klinger, *Tech. Mitt. Krupp*, 3, 1, 1935. For the preparation of phenylarsinic acid, see C. S. Palmer and R. Adams, *Journ. Amer. Chem. Soc.*, 44, 1361, 1922.

[4] Thorium, unlike the rare earths, forms a phenylarsinate insoluble in large excess of acetic acid; thus the reagent can be used for the determination of thorium in monazite sand—A. C. Rice, H. C. Fogg and C. James (*l.c.*). For the use of *n*-propylarsinic acid, see F. W. Arnold, junr., and G. C. Chandlee, *l.c.*; G. C. Chandlee, *Journ. Amer. Chem. Soc.*, 57, 591, 1935; H. H. Geist and G. C. Chandlee, *Ind. Eng. Chem. Anal. Ed.*, 9, 169, 1937.

precipitates basic zirconium selenite, together with hafnium, titanium, thorium and ceric cerium, from faintly acid solution.[1] The solution must not be more than 0·6N in hydrochloric acid nor more than 0·4N in nitric acid, and sulphuric acid and sulphates must be absent. Consequently the hydrochloric or nitric acid solution is diluted to the required acidity, boiled and an excess of a 10 per cent. solution of selenious acid in water added. The solution is kept warm until the precipitate has settled,[2] then filtered and the precipitate washed with hot water. The precipitate is redissolved in hydrochloric acid, the solution diluted and reprecipitated as before.[3] The final precipitate is washed, ignited to ZrO_2 and weighed. Simultaneous separation of titanium and cerium is prevented by the addition of hydrogen peroxide before each precipitation. When thorium is present, it is separated from zirconium by double precipitation as oxalate in hydrochloric acid solution (sulphates must not be present), followed by a third precipitation of the zirconium as basic selenite from the filtrate.

This method does not separate zirconium from phosphates, columbium and tantalum.[4] The inhibition of complete precipitation by sulphuric acid or sulphates is a disadvantage.

§ 277. The Opening-up and Analysis of Zirconium Minerals.

The opening-up of zirconium minerals is often a matter of considerable difficulty, especially when dealing with a mineral such as zircon, $ZrSiO_4$. Among the many fluxes which have been proposed are alkali carbonates,[5] alkali hydroxides [6] with or without alkali fluorides, borax,[7] alkali bisulphates [8]

[1] M. S. Smith and C. James, *Journ. Amer. Chem. Soc.*, 42, 1764, 1920; S. G. Simpson and W. C. Schumb, *ib.*, 53, 921, 1931; *Ind. Eng. Chem. Anal. Ed.*, 5, 40, 211, 1933; 7, 36, 1935.

[2] If warmed for more than about 2 hours, the precipitate becomes crystalline, in which condition it does not readily redissolve in acids.

[3] One precipitation does not entirely eliminate titanium and cerium; also vanadates and uranyl salts, if present, are strongly adsorbed by the zirconium precipitate.

[4] For the separation of zirconium from columbium and tantalum, see W. P. Headden, *Proc. Colorado Sci. Soc.*, 11, 185, 1917; W. R. Schoeller and A. R. Powell, *Journ. Chem. Soc.*, 119, 1927, 1921; *Analyst*, 57, 550, 1932.

[5] F. Wöhler, *Liebig's Ann.*, 31, 122, 1839; P. Berthier, *Ann. Chim. Phys.*, (1), 50, 362, 1832; W. Henneberg, *Journ. prakt. Chem.*, (1), 38, 508, 1846; H. L. Wells and H. W. Foote, *Zeit. anorg. Chem.*, 10, 434, 1895; L. M. Dennis and A. E. Spencer, *Journ. Amer. Chem. Soc.*, 18, 673, 1896; J. Brown, *ib.*, 39, 2358, 1917; C. F. Chandler, *Pogg. Ann.*, 102, 446, 1857; M. Wunder and B. Jeanneret, *Zeit. anal. Chem.*, 50, 733, 1911; M. Wunder and P. Wenger, *ib.*, 51, 470, 1912; P. Wenger and J. Morel, *Ann. Chim. anal.*, 3, 139, 1921; J. D. Ferguson, *Eng. Min. Journ.*, 106, 793, 1918; W. R. Schoeller and A. R. Powell, *Journ. Chem. Soc.*, 119, 1927, 1921; W. R. Schoeller, *Sands, Clays and Minerals*, 2, 7, 1934; H. F. Harwood, *Tids. Kjemi Berg.*, 12, 23, 1932.

[6] M. H. Klaproth, *Beiträge zur chemischen Kenntniss der Mineralkörper*, Berlin, 1, 203, 227, 1795; F. Dubois and A. A. da Silveira, *Ann. Chim. Phys.*, (1), 14, 111, 1820; C. Marignac, *ib.*, (3), 60, 260, 1860; J. J. Berzelius, *Pogg. Ann.*, 4, 117, 1825; E. Melliss, *Bull. Soc. chim.*, (2), 14, 204, 1870; E. Linnemann, *Monats.*, 6, 335, 1885; *Chem. News*, 52, 233, 240, 1885; G. H. Bailey, *ib.*, 53, 55, 260, 287, 1886; 60, 6, 17, 32, 1889; F. P. Venable, *Journ. Amer. Chem. Soc.*, 16, 469, 1894; F. P. Venable and W. Belden, *ib.*, 20, 273, 1898; F. P. Venable and T. Clarke, *ib.*, 18, 434, 1896; *Chem. News*, 74, 44, 1896.

[7] G. E. F. Lundell and H. B. Knowles, *Journ. Amer. Chem. Soc.*, 42, 1439, 1920; W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, New York, 444, 1929.

[8] J. M. Matthews, *Journ. Amer. Chem. Soc.*, 20, 815, 1898; J. L. Smith, *Compt. rend.*, 31, 48, 191, 1850; *Silliman's Journ.*, 10, 354, 1850; M. Dittrich and R. Pohl, *Zeit. anorg. Chem.*, 43, 236, 1905; L. Weiss and R. Lehrmann, *ib.*, 65, 178, 1910; S. J. Johnstone, *The Rare Earth Industry*, 51, 1915; H. F. Harwood, *Tids. Kjemi Berg.*, 12, 23, 1932.

and sodium peroxide.[1] The choice of the flux is not conditioned solely by the ease and rapidity with which it acts, but also by the subsequent analytical procedure, since in certain separations the presence of salts introduced by the flux may be undesirable.

Decomposition of the Material.—Fuse a half or one gram of the dried (110°) mineral, which has been ground to pass a 100 mesh sieve, with about ten times its weight of sodium bisulphate.[2] If the material is very resistant to attack, the fusion must be prolonged for some time.

Determination of Silica.—When cold, extract the cake with 10 per cent. sulphuric acid and digest until it is disintegrated. Evaporate as far as possible on a water bath, then transfer to a sand bath and continue the evaporation until the mass fumes strongly but is still quite pasty. *Cool*, carefully dilute with water so that the temperature does not rise above 40°-50°, filter and wash the impure silica[3] free from sulphates with hot water.[4] Ignite the residue in a platinum crucible and weigh. Fume off the silica by treatment with hydrofluoric and sulphuric acids as usual. Again ignite and weigh. Fuse up the residue with sodium carbonate, extract the cold cake with water, digest, filter and wash free from alkali. The filtrate will contain any phosphorus (also tungsten) present in the mineral as phosphate, which can subsequently be determined by any standard procedure (pages 672 *et seq.*). The insoluble residue from the sodium carbonate fusion is ignited and fused up with a little sodium bisulphate and the solution of the cake in dilute sulphuric acid added to the filtrate from the silica.[5]

Determination of Basic Oxides.—Remove the platinum (also other metals precipitated by hydrogen sulphide in acid solution, if present) by the method given in Section 274. After filtering and washing the precipitate, boil off the hydrogen sulphide, oxidise the filtrate by adding a little concentrated nitric acid and boil off the oxides of nitrogen. From this point onwards the analysis follows that of a typical silicate, zirconium being determined in an aliquot part of the stock solution, obtained from the bisulphate fusion, by one of the methods given in Sections 274 to 276.[6]

§ 278. The Rare Earths.

The term "rare earth" is applied to certain trivalent metallic oxides—yttria and ceria earths—which were formerly regarded as elementary bodies. They fall into the same analytical group as aluminium, iron and beryllium, from which they can be separated as oxalates insoluble in dilute acids and in cold

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[1] A. Travers, *Chim. et Ind.*, **2**, 385, 1919; W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, New York, 445, 1929; S. G. Simpson and W. C. Schumb, *Journ. Amer. Chem. Soc.*, **53**, 930, 1931. Compare G. G. Marvin and W. C. Schumb, *ib.*, **52**, 574, 1930; W. F. Muehlberg, *Ind. Eng. Chem.*, **17**, 690, 1925.

[2] In view of the sparing solubility of the double potassium zirconium sulphates it is better to use sodium rather than potassium bisulphate. For the method of conducting bisulphate fusions, see page 166.

[3] Zirconia is tenaciously retained by silica and the silica residue is almost certain to contain appreciable quantities of zirconium. Partial hydrolysis of zirconium sulphate during the evaporation is a contributory cause of contamination.

[4] G. E. F. Lundell and H. B. Knowles (*Journ. Amer. Chem. Soc.*, **42**, 1439, 1920) warm the filtrate overnight to precipitate any phosphorus as zirconium phosphate. This is subsequently filtered off, washed with 5 per cent. ammonium nitrate and the washings added to the filtrate.

[5] Note, if barium is present it will be separated here as sulphate, which can be filtered off, ignited and weighed.

[6] Any silica, not separated by the single evaporation and filtration, can be recovered at this stage, as indicated on page 167.

ammonium oxalate solutions.   The solubilities of the oxalates[1] of some of these earths in water, in solutions of ammonium oxalate and in sulphuric acid solutions are shown in the following table:—

Table LVII.—Solubilities of the Rare Earth Oxalates.

Oxalate.	Water. Grm. per litre.	Ammonium oxalate. One gram of oxalate in 38 grms. of water dissolves grm.	Normal sulphuric acid. Grms. of anhydrous oxalate per litre.
Lanthanum . . .	0·00062	0·00023	2·56
Praseodymium . .	0·00074	0·00026	1·23
Neodymium . . .	0·00049	0·00034	1·00
Cerium . . .	0·00041	0·00042	1·64
Yttrium . . .	0·00100	0·00256	..
Ytterbium . . .	0·00334	0·02437	..
Thorium . . .	..	0·62000	0·190

G. Urbain classifies the rare earths into three main groups, according to the solubility of their double potassium sulphates in a saturated solution of potassium sulphate.   The classification is as follows:—

1. CERIUM GROUP (insoluble double sulphates).—Lanthanum, La; cerium, Ce; praseodymium, Pr; neodymium, Nd; samarium, Sa; together with thorium, Th, and scandium, Sc, which also form insoluble potassium sulphates, though, strictly speaking, they are not members of the rare earth family.

2. TERBIUM GROUP (moderately soluble double sulphates).—Europium, Eu; gadolinium, Gd; terbium, Tb.

3. YTTRIUM GROUP (readily soluble double sulphates):
   (a) *Ytterbium Sub-group.*—Yttrium, Y; ytterbium, Yb; lutecium, Lu.
   (b) *Erbium Sub-group.*—Dysprosium, Dy; holmium, Ho; erbium, Er; thulium, Tm.

Thorium and zirconium earths are not included in the above definition of the rare earths, but in general analytical work it is often convenient to include both thoria and zirconia with the rare earths, because they have many analogous properties.

While the isolation of individual members of the rare earth family is a matter often of extreme difficulty, it is comparatively easy to separate the group as a whole from other elements.   The amount of the material taken for analysis is conditioned by the amount of rare earths it contains, as the smaller the proportion, the larger must be the analysis sample.

Decomposition of the Mineral.—The mineral must be very finely powdered, and the method adopted for opening it up depends upon its nature.   For

[1] E. Rimbach and A. Schubert, *Zeit. phys. Chem.*, **67**, 183, 1909; B. Brauner, *Journ. Chem. Soc.*, **73**, 951, 1898; O. Hauser and F. Wirth, *Zeit. anal. Chem.*, **47**, 389, 1908; R. J. Meyer and O. Hauser, *Die Analyse der seltenen Erden und Erdsäuren*, Stuttgart, 61, 1912; R. J. Meyer and A. Wassjuchnoff, *Zeit. anorg. Chem.*, **86**, 257, 1914; F. Wirth, *ib.*, **58**, 213, 1908; **76**, 174, 1912; **79**, 357, 1913; **87**, 1, 1914; A. Job, *Compt. rend.*, **126**, 246, 1898; C. James, *Journ. Amer. Chem. Soc.*, **34**, 757, 1912; L. A. Sarver and P. H. M. P. Brinton, *ib.*, **49**, 943, 1927; J. W. Neckers and H. C. Kremers, *ib.*, **50**, 950, 1928; I. M. Kolthoff and R. Elmquist, *ib.*, **53**, 1225, 1931; C. R. Böhm, *Die Verwendung der seltenen Erden*, Leipzig, **5**, 1913; *Pharm. Ztg.*, **47**, 737, 1902.

example, allanite, cerite, gadolinite, thorite and yttrialite are soluble in hydrochloric acid, and sulphuric acid decomposes æschenite, allanite, cerite, euxenite, gadolinite, monazite, thorianite, xenotime and yttrotitanite. Fusion with sodium carbonate has been recommended for decomposing monazite, but sulphuric acid is commonly used. Euxenite, fergusonite, polycrase, samarskite and yttrotantalite are opened up by fusion with sodium bisulphate or pyrosulphate. Sodium hydroxide is the best reagent for attacking some of the columbates, the tantalates and titanates.

When sulphuric and hydrofluoric acids are used, the fluorine is driven off by heating. If hydrochloric acid be used, the solution is evaporated to dryness to make the silica insoluble.[1] The residue is treated with a little hydrochloric acid, diluted with water and filtered. If sulphuric acid, or sodium pyrosulphate or bisulphate, be used for opening the mineral, the mass must be stirred with cold water to get the required solution; otherwise, titanium hydroxide may be precipitated. If hydrofluoric acid alone be used in the cold, a gelatinous precipitate of the silico-fluorides and fluorides of the earths is obtained. The precipitate is collected and washed with dilute hydrofluoric acid. Columbium, tantalum and zirconium pass into solution.[2] The insoluble fluorides are decomposed by sulphuric acid. Fusion of the mineral with sodium or potassium hydroxide or carbonate, and leaching with water, give a residue of insoluble hydroxides.

Removal of Acidic Oxides.—The acid solution of the mineral, obtained by one of the above methods, is evaporated to dryness. The residue is digested with acid, boiled for two hours, stood for some hours and filtered. The residue contains the silica, stannic, tungstic, titanic, columbic and tantalic oxides, together with barium and lead sulphates, if present, and part of the zirconia and ferric oxide. The filtrate contains the alumina, the bulk of the ferric and zirconium oxides, the rare earth oxides, uranium and thorium oxides, and the alkaline earth metals. The filtrate is heated to boiling and saturated with hydrogen sulphide until cold. Any precipitate is filtered off and washed with cold, distilled water, saturated with hydrogen sulphide. The filtrate is boiled to expel the excess of hydrogen sulphide, oxidised with a few c.c. of nitric acid and a double ammonia precipitation is then made in the usual way.

The Separation of Thoria, Ceria and the Yttria Earths from the Ammonia Precipitate.—The ammonia precipitate containing the aluminium, iron, yttrium, cerium, thorium, zirconium and uranium hydroxides or phosphates is dissolved in the smallest possible quantity of hydrochloric acid and the solution is treated with oxalic acid. The yttrium, cerium and thorium oxalates are precipitated, while zirconium, aluminium, iron and uranium[3] remain in solution.[4] The oxalates separate in a colloidal form, containing adsorbed mother liquor.

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[1] H. B. Hicks (*Journ. Amer. Chem. Soc.*, **33**, 1492, 1911; *Chem. News*, **105**, 63, 76, 1912) recommends sulphur monochloride vapour for opening the rare earth minerals. Volatile chlorides are formed. This treatment decomposes rutile, wolframite, scheelite, tantalite and chromite. See also E. F. Smith, *Journ. Amer. Chem. Soc.*, **20**, 289, 1898; R. D. Hall, *ib.*, **26**, 1243, 1904; H. S. Lukens, *ib.*, **35**, 1464, 1913.

[2] M. M. Delafontaine, *Chem. News*, **75**, 229, 1897.

[3] According to O. Hauser (*Zeit. anal. Chem.*, **47**, 677, 1908), the presence of uranyl salts makes the cerium oxalates very soluble, unless a great excess of oxalic acid is added.

[4] The precipitated oxalates will be contaminated with phosphates, if phosphorus compounds be present. A reprecipitation may then be necessary; or the precipitate may be washed into a dish and digested with fuming hydrochloric acid, then warmed with oxalic acid and the whole diluted with water. In this way most of the phosphoric acid passes into solution.

Consequently a portion of the oxalic acid is first added and the solution well shaken until the precipitate in it becomes crystalline, when the remainder of the oxalic acid is added. The metals in the filtrate can be separated by processes previously described. The chief source of difficulty is the fact that the acidity of the solution requires careful adjustment or appreciable quantities of the cerium, yttrium and thorium oxalates will pass into solution or else the precipitate may be contaminated with zirconium oxalate.[1] The conditions for successful work with ceria [2] have been investigated, but not for yttria.[3] The best results are obtained when the ammonia precipitate is dissolved in 0·25N- to 0·5N-hydrochloric acid—about 50 c.c. of acid are required per gram of the earths. Add 40–50 c.c. of a 10 per cent. solution of oxalic acid and keep the solution at about 60° for about 12 hours. Filter and wash with warm water. The precipitated oxalates are usually contaminated with small quantities of aluminium, iron and calcium oxalates and phosphates. Consequently the precipitate is digested with fuming hydrochloric acid on a water bath until it is decomposed and a reprecipitation made with oxalic acid. The precipitate can be calcined to convert the oxalates into oxides and weighed.[4]

If it be desired to separate the thoria, yttria and ceria, the washed precipitate is digested on a water bath with concentrated nitric acid (sp. gr. 1·4) and one drop of 0·1N-potassium permanganate, which accelerates the rate of dissolution by the nitric acid. The dish should be covered with a clock-glass to prevent loss by spurting. The oxalates will be decomposed in a short time. The excess of acid is removed by evaporation and the thorium precipitated by the hydrogen peroxide process (page 567), or by the sodium thiosulphate process.

Separation of Thorium by Sodium Thiosulphate.—The nitrate solution is repeatedly evaporated with hydrochloric acid to convert the nitrates into chlorides (page 464). Dilute the solution and heat it to boiling. Add an excess of a concentrated solution of sodium thiosulphate. Basic thorium thiosulphate is precipitated in a flocculent mass which, after standing about 12 hours, is easily filtered and washed. The precipitate with its filter-paper is digested in concentrated hydrochloric acid and again treated with the thio-

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[1] For the behaviour of zirconium salts with oxalic acid and ammonium oxalate, see J. J. Berzelius, *Schweigger's Journ.*, **21**, 40, 1817; C. H. Pfaff, *ib.*, **28**, 102, 1820; R. Hermann, *Journ. prakt. Chem.*, (1), **95**, 127, 1865; N. J. Berlin, *ib.*, (1), **58**, 145, 1853; R. Ruer, *Zeit. anorg. Chem.*, **42**, 87, 1904; L. N. Vauquelin, *Ann. Chim. Phys.*, (1), **22**, 179, 1797; C. Glaser, *Journ. Amer. Chem. Soc.*, **18**, 782, 1896; F. P. Venable and C. Baskerville, *ib.*, **19**, 12, 1897.

[2] E. Hintz and H. Weber, *Zeit. anal. Chem.*, **36**, 213, 1897; P. Drossbach, *Zeit. angew. Chem.*, **14**, 655, 1901; E. Benz, *ib.*, **15**, 297, 1902; O. Hauser and F. Wirth, *ib.*, **22**, 484, 1909; C. Glaser, *Zeit. anal. Chem.*, **36**, 213, 1897; R. Finkener, *ib.*, **3**, 369, 1864; R. J. Meyer and R. Jacoby, *Zeit. anorg. Chem.*, **27**, 364, 1901; N. Engström, *Zeit. Kryst.*, **3**, 191, 1879; W. Blomstrand, *ib.*, **15**, 99, 1889; H. Bäckström, *ib.*, **16**, 83, 1890; C. Jones, *Amer. Chem. Journ.*, **20**, 345, 1898; H. Gorceix, *Compt. rend.*, **100**, 357, 1885; M. Holzmann, *Journ. prakt. Chem.*, (1), **75**, 321, 1858; R. Ruer, *Zeit. anorg. Chem.*, **42**, 87, 1904; M. Dittrich, *Ber.*, **41**, 4373, 1908; A. Wöber, *Zeit. landw. Versuchw. Oester.*, **20**, 500, 1917; *Chem. Zentr.*, (1), 476, 1918.

[3] L. F. Nilson, *Ber.*, **13**, 1437, 1880; P. T. Cleve and M. Höglund, *ib.*, **6**, 1468, 1873; N. J. Berlin, *Pogg. Ann.*, **43**, 111, 1838.

[4] The results obtained by precipitating the rare earth hydroxides from solution in hydrochloric acid by means of sodium hydroxide or aqua ammonia, washing and igniting, are usually higher than when the earths are precipitated as oxalates and ignited. This is supposed to be due to the adsorption of some alkali, in the case of sodium hydroxide, but also to the formation of a little basic chloride of the rare earth, which is not decomposed by the ignition. With ammonia precipitations from nitrate solutions the results ought to be the same as with the oxalate precipitation since the nitrates are broken down by ignition— T. O. Smith and C. James, *Journ. Amer. Chem. Soc.*, **36**, 909, 1914; *Chem. News*, **109**, 219, 1914.

sulphate so as to get rid of all but a trace of ceria which contaminated the first precipitate. The precipitate is dissolved in hydrochloric acid and treated with oxalic acid as described above.[1] The first filtrate contains the yttrium and cerium earths. The hydroxides are precipitated by ammonia and separated by the double potassium sulphate process described on page 571 for separating zirconium and yttrium. The cerium salt, $3K_2SO_4.Ce_2(SO_4)_3$, is but sparingly soluble, while the yttrium salt, $3K_2SO_4.Y_2(SO_4)_3$, is readily soluble.

No exact quantitative methods are known for separating the individual members of these groups, and all known methods give more or less approximate analytical separations. This is because the reactions of the different members of the group of rare earths, with the possible exception of cerium, differ among themselves only by minute differences; so much so that it is difficult to draw a real line of demarcation even between the yttrium and cerium earths. In all attempts at separation it is necessary to dissolve and reprecipitate a number of times and in some cases an elaborate process of fractional crystallisation must be used. These methods fall outside the range of analytical work and details must be sought in the original memoirs.[2]

§ 279. The Determination of " Rare Earths " in Silicates.

The determination of zirconium in silicates has been discussed on page 554. If rare earths be also present, they will be found in the filtrate from the zirconium. Several methods of separating the rare earths are available. The following process is adapted for silicates containing but small quantities of the rare earths. It is based upon the very sparing solubility of the fluorides of the rare earths and thorium and the ready solubility of the fluorides of the remaining elements (including zirconium, if present) in dilute hydrofluoric acid.[3]

Start with the filtrate from the zirconium phosphate (page 554), which we can suppose contains salts of the rare earths, beryllium, titanium, aluminium, iron and uranium. Treat the solution with an excess of sodium hydroxide, in which beryllium, uranium and aluminium hydroxides are soluble, while titanium, iron and the rare earth hydroxides are almost insoluble. Dilute the solution. Decant the clear liquid through a filter-paper, wash the precipitate twice by decantation and then wash the precipitate into a platinum dish.

Treat the precipitate with hydrofluoric acid, evaporate the mixture nearly to dryness and add a little water with a few drops of hydrofluoric acid. Collect the insoluble precipitated fluorides on a filter-paper, using a rubber funnel and platinum cone. Wash the precipitate with water acidulated with hydrofluoric acid and finally transfer the dried precipitate to a platinum dish.

[1] W. F. Hillebrand and G. E. F. Lundell (*Applied Inorganic Analysis*, New York, 422, 1929) note that the precipitation of thorium by this process is apt to be incomplete and that the separation is not sharp. Ceria is more readily separated than yttria. Furthermore, the inevitable precipitation of sulphur obscures the precipitation of thorium. See P. Drossbach, *Zeit. angew. Chem.*, **14**, 655, 1901.

[2] For a summary of the various methods for separating the rare earths, see J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, London, **5**, 543–576, 1924. See H. T. S. Britton (*Journ. Chem. Soc.*, **127**, 2142, 1925) for the precipitation of the cerite group of metals and of yttrium hydroxide by the use of a hydrogen electrode—the pH values range from 6·83 for samarium to 8·35 for lanthanum. L. M. Dennis and B. J. Lemon, *Journ. Amer. Chem. Soc.*, **37**, 131, 1915; W. Prandtl and J. Rauchenberger, *Zeit. anorg. Chem.*, **120**, 120, 1921; **122**, 311, 1922; **129**, 176, 1923; W. Prandtl and J. Lösch, *ib.*, **127**, 209, 1923. For the determination of cerium and thorium, see J. P. Bonardi, *U.S. Bur. Mines Bull.*, **212**, ii, 19, 1923.

[3] W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **176**, 77, 1900; J. J. Chydenius, *Pogg. Ann.*, **119**, 49, 1861; M. M. Delafontaine, *Chem. News*, **75**, 229, 1897; J. J. Berzelius, *Pogg. Ann.*, **16**, 385, 1829; A. Rosenheim, V. Samter and I. Davidsohn, *Zeit. anorg. Chem.*, **35**, 424, 1903.

Evaporate the precipitate to dryness with sulphuric acid to decompose the fluorides. Ignite the filter-paper separately and add the ash to the contents of the dish. Dissolve the residual sulphates in dilute hydrochloric acid, precipitate the rare earths with ammonia, redissolve the precipitate in hydrochloric acid and evaporate to dryness.

Treat the residue with a few drops of an aqueous solution of oxalic acid, filter and wash the insoluble oxalates. Dry the precipitate, ignite the oxalates, weigh the resulting oxides and report as "rare earths."

§ 280. The Analysis of a Mixture of Rare Earths.

The analysis of a "rare earth mineral" and the separation of some of the more important members of the rare earth group is well illustrated by the following method for the analysis of monazite sands.[1] The analysis occupies about seven days.

1. *The Fusion.*—About a gram [2] of the finely powdered mineral is fused in a platinum crucible with five to six times its weight of sodium pyro- or bi-sulphate.[3] The temperature is raised very gradually to a red heat so as to avoid loss by spurting. The fusion temperature is kept as low as possible to avoid the formation of sparingly soluble basic sulphates. When all is decomposed, the crucible and contents are allowed to cool. The cold cake is taken up with cold water and evaporated to dryness on a sand bath. Digest the residue in 10 c.c. of concentrated sulphuric acid, pour the solution into 200 c.c. of cold water and boil the mixture in a flask with a reflux condenser for two or three hours. Most of the zirconia and ferric oxide dissolve. Silica, titanic, columbic, tantalic, stannic and tungstic oxides are precipitated.[4] Filter. Let the solution stand 24 hours and re-filter if necessary. Wash the precipitate, which may contain the tungstic, stannic, titanic, tantalic and columbic oxides, the silica and part of the zirconia and ferric oxide. The filtrate contains the rare earth oxides, uranium and thorium oxides, alumina, the rest of the zirconia and ferric oxide and the alkaline earths; also any members of the hydrogen sulphide group present.

2. *The Separation of Silica, Stannic, Tungstic, Titanic, Tantalic and Columbic Acids.*—Digest the residue with ammonium sulphide so as to remove the stannic and tungstic oxides (page 438). Filter and wash. The insoluble residue is then digested with a mixture of equal volumes of 10 per cent. sulphuric acid and 3 per cent. hydrogen peroxide.[5] Filter off the silica, wash, ignite and treat with hydrofluoric and sulphuric acids as usual. The silica residue will contain lead and barium, if present, as sulphates.[6] Dilute the filtrate to 200

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[1] C. Glaser, *Journ. Amer. Chem. Soc.*, **18**, 782, 1896; *Chem. Ztg.*, **20**, 619, 1896; *Zeit. anal. Chem.*, **36**, 213, 1897; *Chem. News*, **75**, 145, 157, 1897; G. Chesneau, *Compt. rend.*, **153**, 429, 1911; S. J. Johnstone, *Journ. Amer. Soc. Chem. Ind.*, **33**, 55, 1914; R. J. Carney and E. D. Campbell, *Journ. Amer. Chem. Soc.*, **36**, 1134, 1914; P. Wenger and P. Christian, *Ann. Chim. anal. Chim. appl.*, **4**, 231, 1922. Compare C. James and A. J. Grant, *Journ. Amer. Chem. Soc.*, **38**, 41, 1916.

[2] More frequently between 10 and 30 grms. are taken if some of the rarer of the "rare earths" are to be determined by the process here described.

[3] The sodium salt is preferred to the potassium salt because the latter forms sparingly soluble double sulphates with some of the oxides under investigation.

[4] A trace of tantalic oxide and silica may dissolve in the sodium bisulphate solution. Lead and barium sulphates, if present, remain undissolved.

[5] L. Weiss and M. Landecker, *Zeit. anorg. Chem.*, **64**, 65, 1909.

[6] If any residue is left, fuse with potassium bisulphate. Cold water must be used in dissolving the cake of the bisulphate fusion, the solution being added to the filtrate from the silica.

c.c., add sulphurous acid and boil in a large flask fitted with a reflux condenser (fig. 88) until a little of the clear liquid gives no titanium coloration when tested with hydrogen peroxide. About two or three hours' boiling suffices to precipitate all the titanium, tantalum and columbic oxides. The ferric oxide and zirconia, also any members of the hydrogen sulphide group present, remain in solution. Filter off the insoluble residue and wash. Add the filtrate and washings to the main solution or determine the iron and zirconium they contain as indicated below.

3. *Separation of Titanic Oxide from Columbic and Tantalic Oxides.*—W. R. Schoeller and co-workers recommend the following method.[1] The ignited mixed oxides are fused in a silica crucible with about 12 times their weight of potassium bisulphate. The cold cake is dissolved up in a hot solution of 2 grms. of ammonium oxalate in 250 c.c. of water. 5 grms. of sodium salicylate, dissolved in a little hot water, are added to the boiling solution, followed by a 20 per cent. solution of calcium chloride, added gradually in small portions until all the oxalate is precipitated. Keep the solution hot on a boiling water bath and, after settling, test the supernatant liquid for complete precipitation. Filter under suction, using a platinum cone, and wash the precipitate with a hot 2 per cent. solution of sodium salicylate until the washings are colourless. The oxalate precipitate contains the bulk of the earth acids, while the titania and the small balance of earth acids are present in the yellow filtrate. The oxalate precipitate is dissolved in 40 to 50 c.c. of hydrochloric acid (1 in 1) and the oxalic acid destroyed by the cautious addition to the boiling solution of a slight excess of strong permanganate solution. The excess of the latter is destroyed by further boiling, the solution is diluted to 300 c.c., boiled and the earth acids precipitated by the addition of 1 grm. of tannin in fresh, strong solution. The mixture is boiled for 5–10 minutes, stood for some hours, then mixed with filter-pulp, filtered under gentle suction, the precipitate washed with a 2 per cent. solution of ammonium chloride, containing a little tannin, and ignited in a porcelain crucible. The yellow filtrate from the initial oxalate precipitation is heated and then treated with 10 grms. each of ammonium acetate and ammonium chloride and 1 to 2·5 grms. of a fresh, strong solution of tannin. After settling on a water bath, the precipitate is filtered off under gentle suction and washed with ammonium chloride-tannin solution. The precipitate is ignited in a silica crucible, the residue fused with potassium bisulphate and the cold cake extracted with a hot 1 per cent. solution of tannin in 5 per cent. sulphuric acid. The extract and rinsings from the crucible are boiled and stood overnight in the cold. The small balance of earth acids is filtered off, washed with 5 per cent. sulphuric acid and ignited in the crucible containing the bulk of the earth acids. The weight of the combined residues is reported as $Cb_2O_5 + Ta_2O_5$. The titanium is precipitated from the filtrate by nearly neutralising the diluted solution with ammonia, boiling and adding a large excess of ammonium acetate and ammonium nitrate. The precipitate is washed with ammonium chloride solution, containing a little tannin, ignited, purified by leaching, again ignited and weighed.[2]

4. *Separation of the Hydrogen Sulphide Group.*—Saturate the hot acid filtrates from 1 and 2 with hydrogen sulphide and, when cold, again saturate the solution with the same gas. The members of the hydrogen sulphide group are precipitated. Filter and boil the filtrate to expel the hydrogen sulphide. The residue on the filter-paper contains the metals of the hydrogen sulphide

[1] W. R. Schoeller, *Analyst*, **57**, 72, 1932; *ib.*, **54**, 320, 453, 709, 1929.
[2] For the further purification of the rare earth oxides and the titania, see W. R. Schoeller, (*l.c.*).

group, *e.g.* copper, bismuth. These, if present, are separated as described on page 327.

5. *Separation of the Thorium and Cerium Group from the Zirconium and Yttrium Groups.*-- Thorium oxalate is somewhat soluble in nearly neutral solutions of ammonium oxalate [1] and, if a large excess of ammonium oxalate be used, thorium may not be precipitated at all. But an excess is necessary to keep the zirconium oxalate in solution. Hence some thorium may escape precipitation and, if not separated, will, later on, appear with the zirconium precipitate. Glaser therefore recommended adding concentrated hydrochloric acid to the boiling filtrate. On cooling, insoluble thorium oxalate is precipitated. The zirconium oxalate is soluble in the oxalic acid liberated by the action of the hydrochloric acid.[2]

The method here used is based on the solubility of yttrium and zirconium oxalates and the "insolubility" of thorium and cerium oxalates in slightly mineral acid solutions, containing an excess of oxalic acid. An alternative process is indicated on page 562.[3] Dilute the filtrate and washings from the preceding operation until not more than 2 per cent. by volume of free sulphuric acid is present. Pour the diluted solution very slowly and with constant stirring into 150 c.c. of a cold saturated solution of oxalic acid. Stand overnight, filter and wash the precipitate with cold 1 per cent. hydrochloric acid. Reserve the precipitate. Just neutralise the filtrate and washings with ammonium hydroxide and redissolve the precipitate in 10 c.c. of concentrated hydrochloric acid. Again stand overnight, filter and wash with a solution containing 4 per cent. by volume of hydrochloric acid and 2·5 per cent. by weight of oxalic acid. Ignite the precipitate, redissolve it in 10 c.c. of hydrochloric acid and filter if necessary. Dilute the solution to 500 c.c. and to it gradually add 100 c.c. of a hot 10 per cent. solution of oxalic acid. Allow to cool for several hours, filter and wash with the hydrochloric-oxalic wash liquor as before. Combine with the reserved precipitate and ignite.[4] The ignited precipitate contains the thorium, cerium, lanthanum and "didymium" as oxides.[5] The filtrate is reserved for the determination of phosphorus, aluminium, iron, manganese, yttrium, zirconium and alkaline earths.

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[1] J. F. Bahr, *Liebig's Ann.*, **132**, 231, 1864.

[2] But even with Glaser's improvement the operation is not altogether satisfactory. The thorium and zirconium may be first removed by Metzger's process and the thorium and zirconium separated by the oxalic acid process. The method given here is that recommended by W. F. Hillebrand and G. E. F. Lundell (*Applied Inorganic Analysis*, New York, 418, 1929).

[3] The presence of uranium salts augments the solubility of cerium and lanthanum oxalates and therefore the precipitation will be imperfect in the presence of uranium salts, unless a large excess of oxalic acid is added—O. Hauser, *Zeit. anal. Chem.*, **47**, 665, 1908.

[4] See footnote 7, page 567, if thorium is subsequently to be separated from cerium earths.

[5] E. Hintz and H. Weber, *Zeit. anal. Chem.*, **36**, 27, 1897; P. Drossbach, *Zeit. angew. Chem.*, **14**, 655, 1901; E. Benz, *ib.*, **15**, 297, 1902; T. Scheerer, *Pogg. Ann.*, **56**, 498, 1842; **51**, 470, 1840; C. Rammelsberg, *ib.*, **108**, 48, 1859; H. Rose, *ib.*, **118**, 502, 1863; T. Thomson, *Trans. Roy. Soc. Edin.*, **6**, 371, 1811; A. Connell, *Edin. Phil. Journ.*, **20**, 300, 1842; R. Hermann, *Journ. prakt. Chem.*, (1), **82**, 387, 1861; M. Holzmann, *ib.*, (1), **84**, 78, 1861; T. Lange, *ib.*, (1), **82**, 135, 1861; M. M. Delafontaine, *Liebig's Ann.*, **131**, 105, 1864; J. Brush and S. L. Penfield, *Amer. J. Science*, (3), **25**, 459, 1883; G. Bodmann, *Zeit. anorg. Chem.*, **27**, 254, 1901; H. du Bois and O. Liebknecht, *Ber.*, **32**, 3346, 1899. If much yttrium earths be present, the precipitate may be contaminated with them. The precipitate is then redissolved and the operations repeated. A similar remark applies if phosphorus be present.

I. *The Ammonium Oxalate Precipitate.*

6. *Separation of Thorium from Cerium, Lanthanum and "Didymium."* [1]— This separation is based on the solubility of thorium oxalate, and the "insolubility" of cerium, lanthanum and "didymium" oxalates, in a solution of ammonium oxalate containing a little ammonium acetate. A large excess of ammonium acetate should not be used, because cerium oxalate is slightly soluble in that reagent. When an excess of ammonium oxalate is present, a few c.c. of a solution of ammonium acetate will suffice to keep the thorium oxalate in solution.

Dissolve the mixed oxides [2] in sulphuric acid, and just neutralise with ammonia. Add to the boiling solution an excess of a boiling solution of ammonium oxalate. In a short time, when the oxalates of the cerium earths have formed and before the liquid has cooled, add a solution of ammonium acetate.[3] Cerium oxalate will be precipitated, while thorium oxalate remains in solution. Let the solution stand overnight. Filter and wash. Dissolve the precipitate in nitric acid and repeat the treatment, since otherwise some thorium will be precipitated and, later, contaminate the cerium.[4]

7. *Determination of Thorium.*—Add an excess of ammonia to the filtrate, and thorium hydroxide will be precipitated. It is the general rule, in separating the rare earths in the presence of alkali solutions, to dissolve the hydroxide and reprecipitate, since the hydroxides are particularly liable to adsorb alkali salts from the mother liquid. The thorium hydroxide may be purified by dissolving the precipitate, well washed in boiling water, in nitric acid. Neutralise the solution with ammonia; add 10 grms. of ammonium nitrate [5] per 100 c.c. of solution; heat the solution to between 60° and 80°; add 20 c.c. (per 100 c.c. of solution) of a 10 per cent. solution of hydrogen peroxide [6]; and boil the solution for a few minutes. A flocculent precipitate of thorium hydroperoxide—$Th(O_2H)(OH)_3$—separates. This can be easily washed.[7] Test some of the filtered solution by another treatment with an equal volume of hydrogen peroxide and boil. If no precipitate appears, filter the main solution while hot as rapidly as possible—and wash with a hot 5 per cent. solution of ammonium nitrate. The precipitate should be white.[8] If the precipitate has a yellow tinge, a little ceria may be present. In this case the precipitate

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[1] The term "didymium" is here used for a mixture of praseodymium and neodymium.

[2] The oxalates, obtained in the preceding separation, can be directly dissolved in excess of nitric acid, without prior ignition to oxides, and the solution evaporated to dryness.

[3] If the ammonium acetate be added before the oxalate precipitate has formed, the mixture is inclined to give a turbid filtrate.

[4] E. Hintz and H. Weber, *Zeit. anal. Chem.*, 36, 27, 1897; E. Benz, *Zeit. angew. Chem.*, 15, 297, 1902. For the solubility of thorium oxalate, see R. Bunsen, *Pogg. Ann.*, 155, 380, 1875. E. Benz says that "under no circumstances is it possible to get a satisfactory separation of thorium from cerium by ammonium oxalate in the presence of ammonium acetate." If there is any difficulty, use Metzger's process, page 572.

[5] If the ammonium nitrate be omitted, it is so difficult to calcine the voluminous gelatinous precipitate without loss of fine dust, that it is advisable to dissolve the precipitate in hydrochloric acid and reprecipitate with ammonia.

[6] Traces of phosphoric oxide and cerium, if present, will be precipitated as cerium phosphate with the thorium. If an appreciable time elapses between the precipitation and the filtration of the thorium hydroperoxide, the greater the risk of contamination with ceria.

[7] This behaviour with hydrogen peroxide distinguishes thorium and zirconium from cerium and yttrium compounds.

[8] P. T. Cleve, *Bull. Soc. chim.*, (2), 43, 53, 1885; G. Wyrouboff and A. Verneuil, *ib.*, (3), 19, 219, 1898; *Chem. News*, 77, 245, 1898; *Compt. rend.*, 126, 340, 1898; 127, 412, 1898; 128, 1331, 1899; L. de Boisbaudran, *ib.*, 100, 605, 1885; E. Benz, *Zeit. angew. Chem.*, 15, 297, 1902. For another method of purifying the thorium oxide, see page 572—Metzger's process.

must be redissolved in nitric acid [1] and again precipitated from its neutral solution as in the first instance. The precipitate is finally ignited in a platinum crucible and weighed as thorium oxide—ThO_2.

8. *Separation of Cerium from Lanthanum and "Didymium."*—Dissolve the oxalates of the cerium earths in nitric acid, add the solution to the filtrate and washings from the thorium separation and boil to expel excess hydrogen peroxide. Add a slight excess of sodium hydroxide to precipitate the gelatinous hydroxides of cerium, lanthanum and "didymium." The precipitated earth acids may here be filtered off, washed, ignited and weighed as "cerium earths." This weight would then include lanthana and "didymia." To separate the cerium,[2] wash the precipitated hydroxides three or four times by decantation, dissolve them in the minimum excess of hydrochloric acid, neutralise the solution with potassium hydroxide and add about 2 grms. in excess. Dilute the solution to about 200 c.c. and pass a slow current of chlorine gas through the solution, agitating the mixture from time to time. When the liquid no longer has an alkaline reaction and is saturated with chlorine, the cerium hydroxide will have been oxidised to lemon-yellow cerium dioxide, which remains as an insoluble precipitate, whereas the lanthanum and " didymium " hydroxides will have dissolved.[3] Boil for a few minutes, dilute with an equal bulk of water and let the mixture stand in a corked flask for 24 hours. Filter and wash the cerium dioxide with hot water. While the precipitate is still moist, dissolve it in hydrochloric acid and repeat the whole precipitation.[4] Dissolve the second precipitate in hydrochloric acid and add ammonium oxalate to the solution. Wash and ignite the precipitated cerium oxalate and weigh as cerium oxide—CeO_2. Cerium oxide has a light rose colour and it dissolves in sulphuric acid, giving a yellow solution. The colour is bleached by the addition of sulphurous acid and restored by the addition of hydrogen peroxide or sodium peroxide.[5]

9. *Determination of Lanthanum and " Didymium."*—Owing to the laborious nature of the process for the separation of these bases, they are often precipitated together as oxalates in the filtrate from the cerium dioxide, calcined and

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[1] White thorium hydroxide, $Th(OH)_4$, readily dissolves in ordinary mineral acids; the oxide, ThO_2, is practically insoluble in these acids, but it dissolves in hot fuming sulphuric acid and it can be converted into a soluble sulphate by fusion with sodium pyrosulphate.

[2] G. Mosander, *Journ. prakt. Chem.*, (1), **30**, 276, 1843; H. St C. Deville, *Compt. rend.*, **59**, 272, 1864; P. Schützenberger, *Compt. rend.*, **120**, 663, 962, 1143, 1895; **124**, 481, 1897.

[3] O. Popp (*Liebig's Ann.*, **131**, 359, 1864) used sodium hypochlorite in place of chlorine gas for the separation; W. Gibbs (*Zeit. anal. Chem.*, **3**, 396, 1864) oxidised the solution with lead peroxide; H. Zschiesche (*ib.*, **9**, 541, 1870), red lead; C. Winkler (*ib.*, **4**, 417, 1865; E. J. Roberts, *Amer. J. Science*, (4), **31**, 350, 1911), potassium permanganate; O. N. Witt (*Chem. Ind.*, **11**, 19, 1896), sodium peroxide; G. Wyrouboff and A. Verneuil (*Bull. Soc. chim.*, (3), **19**, 219, 1898; *Chem. News*, **77**, 245, 1898), hydrogen peroxide; L. Haber (*Monats.*, **18**, 693, 1897), W. Muthmann and H. Rölig (*Ber.*, **31**, 1720, 1898), P. E. Browning and E. J. Roberts (*Amer. Journ. Sci.*, (4), **29**, 45, 1910) and S. J. Johnstone (*Journ. Soc. Chem. Ind.*, **33**, 55, 1914), bromine. G. Bricout (*Compt. rend.*, **118**, 145, 1894) suggested a separation based on the solubility of cerium carbonate in chromic acid; M. M. Pattison and J. Clarke (*Chem. News*, **16**, 259, 1867) decomposed the chromate by heat; and H. Robinson (*ib.*, **54**, 229, 1886) based a process on the different solubilities of the nitrates.

[4] It is said that even 5 to 10 reprecipitations fail to remove entirely the associated rare earths.

[5] For the detection of cerium, see F. Wirth, *Chem Ztg.*, **37**, 773, 1913; F. Feigl, *ib.*, **44**, 689, 1920; *Chem. Zentr.*, (4), 592, 1919; L. Fernandes, *Gazz. Chim. Ital.*, **55**, 616, 1925; J. Lukas and A. Jilek, *Zeit. anal. Chem.*, **76**, 348, 1929; *Chem. Listy*, **23**, 417, 1929; A. S. Komarovskii and S. M. Korenmann, *Mikrochem.*, **12**, 211, 1932; F. M. Shemyakin, *Zeit. anorg. allgem. Chem.*, **217**, 272, 1934; J. F. Miller, *Ind. Eng. Chem. Anal. Ed.*, **9**, 181, 1937.

weighed as a mixture of "$La_2O_3 + Di_2O_3$."[1] Damour and Deville's process[2] of separation is based on the fact that, when a mixture of "didymium" and lanthanum nitrates is heated, the "didymium" nitrate decomposes before the lanthanum nitrate and forms a sparingly soluble "didymium subnitrate."[3]

The filtrate from the cerium dioxide is boiled to eliminate the chlorine and treated with an excess of ammonia. The precipitated "didymium" and lanthanum hydroxides are washed and dissolved in nitric acid. The solution is evaporated to dryness in a small platinum basin. The dried mass usually
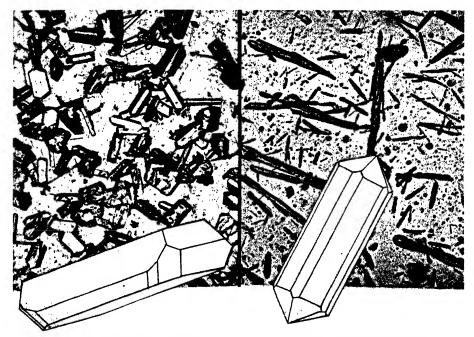
FIG. 116.—"Didymium" Sulphate.   FIG. 117.—Lanthanum Sulphate.

has a pale rose colour. Heat the basin to a temperature of about 450° in a small muffle.[4] Care must be taken not to overheat the mixed salts near the bottom of the basin. The salts fuse and give off nitrous fumes. It is difficult to ensure uniform heating if a large quantity of the mixed nitrates is being treated. The result is better when small quantities are treated. In about half a minute remove the basin from the source of heat. When nearly cold, add hot water. The lanthanum nitrate dissolves, while greenish-grey flakes of "didymium" subnitrate remain undissolved. After the mixture has stood a couple of hours, boil and filter. If the filtrate has a pink colour, evaporate

[1] See footnote 1, page 567.

[2] A. A. Damour and H. St C. Deville, *Bull. Soc. chim.*, (2), **2**, 339, 1864; P. Schützenberger and O. Boudouard, *Compt. rend.*, **122**, 697, 1896; **123**, 782, 1896; **126**, 1648, 1898; L. F. Nilson, *ib.*, **88**, 642, 647, 1879.

[3] A suspension of lanthanum hydroxide in dilute potash on treatment with bromine water dissolves far more readily than the hydroxides of neo- and praseo-dymium, and hence P. E. Browning (*Compt. rend.*, **158**, 1679, 1914) recommends a triple application of this process for the separation of lanthanum from the "didymiums." The method is quicker but not so exact as the fractional crystallisation of the double ammonium nitrates of the metals.

[4] A small electric furnace with a pyrometer is excellent for the purpose.

again with nitric acid and repeat the operation until a colourless liquid is obtained. Two or three repetitions of the process may suffice. According to Cleve, a repetition of the process fourteen times will give a solution in which the spectroscope can detect no "didymium." The "didymium" subnitrate is calcined until its weight is constant and weighed as "didymium" oxide—Di_2O_3. The "didymia" so obtained varies in tint from pure white to pale cinnamon brown—usually a pale yellowish-brown oxide is obtained which is readily soluble in dilute nitric acid.

The lanthanum solution is also evaporated to dryness in a weighed dish, the residue ignited and weighed as oxide--La_2O_3. A slight trace of lanthanum nitrate may be decomposed when the nitrates are calcined; as a result, the amount of "didymia"--Di_2O_3--reported above is usually a little high and the lanthana—La_2O_3--a little low. The lanthanum oxide generally has a pale yellowish-brown colour (if pure it would be white) and it is soluble in acids— e.g. dilute nitric acid.

When "didymium" oxide is treated with sulphuric acid, reddish-violet crystals (oblique rhomboidal prisms) of "didymium" sulphate (fig. 116) are obtainable, while lanthanum sulphate gives colourless needles (right rhomboidal prisms) (fig. 117). Ideally perfect crystals are also shown in outline. Some needles of lanthanum sulphate can usually be detected among the plates of "didymium" sulphate, and conversely.[1]

II. *The Filtrate from the Ammonium Oxalate Precipitate.*

10. *Determination of Aluminium and Phosphorus.*--Add an excess of ammonia to the solution [2] remaining after the separation of the oxalates of the thorium and cerium groups. Filter and wash the precipitated hydroxides and phosphates. The filtrate may contain traces of cerium and thorium, which are usually neglected. The washed precipitate is dried and fused with sodium carbonate. The cold cake is extracted with water. Filter off and wash the insoluble residue. The solution contains sodium phosphate and sodium aluminate. Bring the solution to a definite volume, and determine the phosphorus in one portion (page 672), and the combined aluminium and phosphoric oxides in another (page 164).

11. *Determination of Calcium.*—Dissolve the insoluble residue left, after leaching the sodium carbonate fusion with water, in dilute hydrochloric acid.[3] Add ammonia, filter and wash. Precipitate the lime as calcium oxalate from the filtrate in the usual manner (page 202).

12. *Determination of Iron and Manganese.*--Dissolve the precipitate in hot dilute hydrochloric acid and neutralise the solution with dilute ammonia. Pour the solution slowly, with constant stirring, into a cold mixture of ammonium carbonate and sulphide.[4] Iron and manganese sulphides are precipitated,

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[1] For the separation of lanthanum from other metals of the cerium group by electrolysis, see J. W. Neckers and H. C. Kremers, *Journ. Amer. Chem. Soc.*, 50, 950, 1928. For the analysis of lanthanum, see A. M. Vasil'ev, *Uchenuie Zapiski Kazan Gosudarst Univ.*, 90, 997, 1930. For the separation of neodymium from beryllium, titanium, uranium and barium by precipitation as oxalate, see T. O. Smith and C. James, *Chem. News*, 107, 205, 1913.

[2] This solution may contain aluminium, phosphorus, iron, manganese, calcium, magnesium, beryllium, zirconium and yttrium.

[3] To make sure that all the zirconium is dissolved, incinerate the filter-paper and fuse with a little sodium carbonate. Take up in acid and add the solution to the main solution.

[4] The amount of ammonium carbonate should more than suffice to retain the oxides of yttrium, beryllium and zirconium in solution; and the ammonium sulphide should suffice to precipitate all the iron and manganese.

while zirconium, beryllium and yttrium remain in solution. The precipitated iron and manganese sulphides can be separated in the usual manner.

13. *Separation of Beryllium from Zirconium and Yttrium.*—Boil the filtrate for an hour [1]; beryllium, zirconium and yttrium hydroxides are precipitated. Filter and wash. Dissolve the precipitate in dilute hydrochloric acid.[2] Treat the cold solution with an excess of sodium hydroxide, when zirconium and yttrium hydroxides are precipitated. The beryllium remains in solution. Boil the diluted filtrate one hour, when beryllium hydroxide is precipitated. Wash the precipitate and treat as described on page 493.

14. *Separation of Zirconium and Yttrium.*— This separation [3] is based on the fact that potassium yttrium sulphate, $3K_2SO_4.Y_2(SO_4)_3$, is soluble in 7 to 8 parts of a feebly acid solution of potassium sulphate, while the corresponding potassium zirconium sulphate is practically insoluble in the same menstruum.[4] The operation is conducted in the following manner:—Dissolve the precipitate [5] containing the mixed zirconium and yttrium hydroxides in a little concentrated sulphuric acid.[6] Stir the ice-cold solution with a saturated solution of potassium sulphate.[7] This precipitates a basic double potassium zirconium sulphate [8] possibly $Zr_2O_3(KSO_4)_2.8H_2O$—which is practically insoluble in ice-cold water and in solutions of potassium sulphate. Filter [9] and wash with an ice-cold solution of potassium sulphate. The double sulphate is decomposed by boiling with a concentrated solution of sodium hydroxide. The compact zirconium hydroxide is washed, first by decantation and then on the filter-paper. The precipitate is dissolved in hydrochloric acid,[10] re-precipitated with ammonia, filtered, washed, ignited and weighed as zirconia -ZrO_2 (page 555).

The filtrate from the potassium zirconium sulphate is treated with an excess of ammonia.[11] The precipitate is filtered, washed, dissolved in acid, reprecipitated with ammonia, washed, ignited and weighed as yttria—Y_2O_3. The yttria so obtained is usually pale straw-yellow (if pure, it would be white) and soluble in warm acids.

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[1] Or add hydrochloric acid to the solution and boil to expel the carbon dioxide. Cool and treat the solution with sodium hydroxide as indicated below.

[2] Incinerate the filter-paper and treat the ash as indicated in footnote 3, page 570.

[3] J. J. Berzelius, *Pogg. Ann.*, **4**, 135, 1825; C. M. Warren, *ib.*, **102**, 449, 1857; E. Linnemann, *Monats.*, 6, 335, 1885; C. Marignac, *Ann. Chim. Phys.*, (5), **20**, 535, 1880; *Compt. rend.*, **90**, 899, 1880; *Chem. News*, **41**, 250, 1880; M. M. Delafontaine, *ib.*, **11**, 241, 253, 1865; G. Krüss, *ib.*, **64**, 65, 75, 100, 120, 1891; *Liebig's Ann.*, **265**, 1, 1891; G. Urbain, *Ann. Chim. Phys.*, (6), **19**, 184, 1900.

[4] When zirconia compounds are fused with potassium bisulphate, the insoluble double sulphate remains behind when the cold cake is extracted with water. Neither sodium nor ammonium sulphate can be used in place of the potassium salt, because they do not give a sparingly soluble double salt.

[5] Incinerate and treat the filter-paper ash as indicated in footnote 2 above.

[6] Sulphuric acid is preferable to nitric and hydrochloric acids, since, if chlorides or nitrates be present, some yttrium may be precipitated.

[7] POTASSIUM SULPHATE.—The finely powdered salt is ground in a mortar with water at about 30°, but not at a higher temperature.
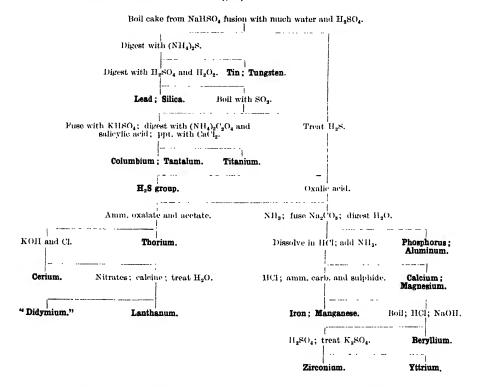
[8] The corresponding sodium and ammonium salts are fairly soluble in water.

[9] The precipitate sometimes sticks tenaciously to the sides of the beaker.

[10] The filter-paper is incinerated, etc., as usual.

[11] C. Kersten, *Pogg. Ann.*, **47**, 392, 1839; H. Rose, *ib.*, **118**, 508, 1863; R. Fresenius and E. Hintz, *Zeit. anal. Chem.*, **35**, 532, 1896; O. Boudouard, *Bull. Soc. chim.*, (3), **19**, 11, 1898; G. Krüss and L. F. Nilson, *Ber.*, **20**, 1677, 1887. According to C. F. Whittemore and C. James (*Journ. Amer. Chem. Soc.*, **34**, 772, 1912) the precipitation of yttrium hydroxide by sodium or ammonium hydroxide gives high results in the presence of potassium or sodium salts; they recommend one precipitation with ammonium sebacate in the presence of sodium salts and two precipitations in presence of potassium salts.

The scheme of analysis may now be summarised (precipitates and solids on left, filtrates and solutions on right):—

Boil cake from NaHSO₄ fusion with much water and H₂SO₄.

Digest with (NH₄)₂S.

Digest with H₂SO₄ and H₂O₂.   **Tin ; Tungsten.**

Lead ; Silica.   Boil with SO₂.

Fuse with KHSO₄ ; digest with (NH₄)₂C₂O₄ and   Treat H₂S.
salicylic acid ; ppt. with CaCl₂.

Columbium ; Tantalum.   Titanium.

H₂S group.   Oxalic acid.

Amm. oxalate and acetate.   NH₃ ; fuse Na₂CO₃ ; digest H₂O.

KOH and Cl.   **Thorium.**   Dissolve in HCl ; add NH₃.   **Phosphorus ;
Aluminum.**

Cerium.   Nitrates ; calcine ; treat H₂O.   HCl ; amm. carb. and sulphide.   **Calcium ;
Magnesium.**

"Didymium."   Lanthanum.   **Iron ; Manganese.**   Boil ; HCl ; NaOH.

H₂SO₄ ; treat K₂SO₄.   **Beryllium.**

Zirconium.   Yttrium.

§ 281. The Gravimetric Determination of Thorium— Metzger's Process.

Metzger's process [1] is based on the fact that a saturated solution of fumaric acid in 40 per cent. alcohol quantitatively precipitates white flocculent thorium

[1] F. J. Metzger, *Journ. Amer. Chem. Soc.*, **24**, 901, 1902. A. C. Neish (*Journ. Amer. Chem. Soc.*, **26**, 780, 1904; *Chem. News*, **90**, 196, 201, 1904; A. Kolb and H. Ahrle, *Zeit. angew. Chem.*, **18**, 92, 1905) separated thorium by metanitrobenzoic acid; L. M. Dennis and F. L. Kortright (*Amer. Chem. Journ.*, **16**, 79, 1894; *Journ. Amer. Chem. Soc.*, **18**, 947, 1896; T. Curtius and A. Darapsky, *Journ. prakt. Chem.*, (2), **61**, 408, 1900), by sodium azide—NaN₃; J. J. Chydenius (*Pogg. Ann.*, **119**, 45, 1861; R. Fresenius and E. Hintz, *Zeit. anal. Chem.*, **35**, 525, 1896; G. P. Drossbach, *Zeit. angew. Chem.*, **14**, 656, 1901; E. Benz, *ib.*, **15**, 302, 1902; O. Hauser and F. Wirth, *ib.*, **22**, 484, 1909; S. J. Johnstone, *Journ. Soc. Chem. Ind.*, **33**, 55, 1914), by boiling with sodium thiosulphate; T. O. Smith and C. James (*Journ. Amer. Chem. Soc.*, **34**, 281, 1912), by sebacic acid; M. Koss (*Chem. Ztg.*, **36**, 686, 1912; A. Rosenheim, *ib.*, **36**, 821, 1912; F. Wirth, *Zeit. angew. Chem.*, **25**, 1678, 1912; *Chem. Ztg.*, **37**, 773, 1913; F. Hecht, *Zeit. anal. Chem.*, **75**, 28, 1928), by sodium hypophosphate; A. Kolb (*Journ. prakt. Chem.*, (2), **66**, 59, 1903), by aniline; R. J. Meyer and M. Speter (*Chem. Ztg.*, **34**, 306, 1910; R. J. Meyer, *Zeit. anorg. Chem.*, **71**, 65, 1911), by potassium iodate; F. Garelli and G. A. Barbieri (*Zeit. angew. Chem.*, **19**, 895, 1906; *Chem. Ztg.*, **30**, 433, 1906; C. R. Böhm, *Chem. Ind.*, **29**, 452, 1906), by salicylic acid; W. M. Thornton (*Amer. Journ. Sci.*, (4), **42**, 151, 1916; N. I. Mateev, *Zhur. Prikladnoi Khim.*, **4**, 275, 1931), by cupferron; F. Hecht and W. Reich-Rohrwig (*Monats.*, **53** and **54**, 596, 1929) by 8-hydroxyquinoline; J. Kotá (*Chem. Listy*, **27**, 79, 100, 128, 150, 194, 1933), by selenic acid; W. B. Giles (*Chem. News*, **92**, 1, 1905; A. C. Neish and J. W. Burns, *Can. Chem. Met.*, **5**, 69, 1921) by lead carbonate. See also B. L. Hartwell, *Journ. Amer. Chem. Soc.*, **25**, 1128, 1903; *Chem. News*, **89**, 15, 27, 1904. Thorium

oxide from neutral solutions containing 40 per cent. alcohol by volume. The only other metals precipitated are zirconium (completely), erbium (partially), silver and mercury. The trial results are excellent. Cerium,[1] lanthanum, "didymium," yttrium, samarium and gadolinium give no precipitates in hot or cold solutions under the same conditions. Similarly with salts of copper, gold, manganese, calcium, strontium, barium, zinc, cadmium, boron, aluminium, tin, lead, phosphorus, arsenic, antimony, bismuth, uranium, vanadium, tungsten, iron, cobalt, nickel, platinum.

First Precipitation.—The precipitated oxalates (page 566) are washed and rinsed into a beaker, mixed with 20-25 c.c. of concentrated caustic potash and boiled. Dilute the solution with water, filter and wash. Dissolve the precipitated hydroxides in dilute nitric acid (1 : 1) and evaporate the solution to dryness on a water bath. Dissolve the residue in 50 c.c. of water and add sufficient alcohol and water to give 200 c.c. of solution, containing 40 per cent. of alcohol by volume. Add 20 to 25 c.c. of fumaric acid [2] and heat the solution to boiling. Filter while hot and wash the precipitated thorium several times with hot 40 per cent. alcohol.

Second Precipitation.—Return the filter-paper and the precipitate to a beaker. Add 25-30 c.c. of dilute hydrochloric acid (1 : 1). Heat the solution to boiling and filter off the paper. Wash with dilute acid and evaporate the filtrate and washings to dryness on a water bath. Agitate the solution and wash down the sides of the basin, every now and again, to prevent the residue clinging to the sides. While still on the water bath, loosen the residue from the bottom of the basin by stirring with a "policeman." The carbonaceous matter does not interfere. Add sufficient 40 per cent. alcohol to make the solution occupy about 150 c.c., add 10 c.c. of fumaric acid solution and heat to boiling. Filter and wash with 40 per cent. alcohol. Ignite and weigh as thorium oxide $-ThO_2$.

Evaluation of Thorium Minerals.[3] The thorium minerals are evaluated on their thorium contents. Most of the commercial thoria comes from monazite sand, which has about 6 per cent. of ThO_2; a little comes from thorianite, which has about 80 per cent. of ThO_2. The following process of evaluation has been tacitly recognised by buyer and seller as a kind of standard :—

Heat 12·5 grm. of the sand to 180°–200° with 50 c.c. of concentrated sulphuric acid.[4] In 2 or 3 hours the grains will be all broken up. Dilute the cold mixture with 300–400 c.c. of water and filter. Make the solution up to 500 c.c. Agitate 200 c.c. (5 grms. of sample) with 180 c.c. of a cold saturated solution of oxalic acid. Let stand overnight (about 12 hours) and filter. Wash the precipitate with dilute hydrochloric acid or water until the runnings are free from phosphates. Reject the filtrates. Ignite the dried precipitate and dissolve it in hydrochloric acid (sp. gr. 1·16). Evaporate to dryness, add a few c.c. of water and again evaporate to dryness. Dissolve the acid-free chlorides in 200 c.c. of water and add 9 grms. sodium thiosulphate in 30 c.c. of water.

is precipitated quantitatively by ammonium molybdate—F. J. Metzger and F. W. Zons, *Journ. Ind. Eng Chem.*, **4**, 493, 1912. R. J. Carney and E. D. Campbell (*Journ. Amer. Chem. Soc.*, **36**, 1134, 1914) find that sodium pyrophosphate precipitates thorium, ceric cerium and zirconium pyrophosphates in 0·3N-hydrochloric or sulphuric acid solution, while cerous cerium and the other rare earths give readily soluble pyrophosphates.

[1] If much cerium be present, a little may be precipitated during the first precipitation of the thorium oxide.

[2] FUMARIC ACID SOLUTION.—Dissolve 1 grm. of fumaric acid in 100 c.c. of water.

[3] E. White, *Thorium and its Compounds*, London, 1912; O. R. Böhm, *Die Fabrikation der Glühkörper für Gasglühlicht*, Halle a. S., 1910.

[4] M. M. Delafontaine (*Chem. News*, **75**, 230, 1897) opens up thorite by fusion with potassium hydrogen fluoride, whereby the rare earths are obtained as fluorides insoluble in dilute hydrofluoric acid; the fluorides are subsequently converted into sulphates.

After standing 12 hours, boil for 10 minutes, filter and wash the precipitate until ammonia gives no turbidity. Boil the filtrate for an hour and collect the precipitate A as before. Reject the filtrate. The first precipitate is dissolved in 5 per cent. hydrochloric acid. The acid solution is evaporated to dryness, taken up with 150 c.c. of water and treated with 3 grms. of sodium thiosulphate as before. The filtrate is treated with ammonia and boiled. The precipitate is washed and mixed with A. The thiosulphate precipitate is dissolved in acid, the solution evaporated and treated with thiosulphate as before. The precipitate is washed until it gives no turbidity with ammonia. The filtrate is precipitated with ammonia, while the thiosulphate precipitate is again subjected to the preceding treatment until the filtrate gives no precipitate with ammonia. Three thiosulphate reprecipitations generally suffice. The last thiosulphate precipitate is dissolved in 5 per cent. hydrochloric acid and the solution made up to 150 c.c.; 10 c.c. of concentrated hydrochloric acid are added and then 30 c.c. of saturated oxalic acid solution. The liquid is kept between 30° and 40° for 2 to 3 hours and, after standing overnight, filtered, washed, dried, ignited and weighed as ThO_2. The ammonia precipitates and the precipitate A are mixed and re-worked for thoria. The yield from the re-working is about 0·005 grm., or 0·1 per cent., on the 5 grm. sample.[1]

§ 282. The Volumetric Determination of Cerium – Knorre's Process.

Cerium can be determined volumetrically in the presence of thorium, lanthanum and "didymium," by Knorre's process.[2] This is based on the fact that cerous salts are oxidised to yellow ceric salts by the action of ammonium persulphate in sulphuric acid solution, and the ceric salts are reduced to colourless cerous salts by the action of hydrogen peroxide:

$$2CeO_2 + H_2O_2 = Ce_2O_3 + O_2 + H_2O$$

If, therefore, an excess of a solution of hydrogen peroxide of known strength be added to the yellow ceric salt, the excess of hydrogen peroxide can be determined by back titration with potassium permanganate. With freshly prepared solutions of the ceric salts, the reduction with hydrogen peroxide is instantaneous and the permanganate is also decolorised at once. With

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[1] For the analysis of monazite, see J. C. H. Mingaye, *Records Geol. Sur. N.S. Wales*, **8**, 276, 1909; C. Glaser, *Journ. Amer. Chem. Soc.*, **18**, 782, 1896; R. J. Carney and E. D. Campbell, *ib.*, **36**, 1134, 1914; F. J. Metzger and F. W. Zons, *Journ. Ind. Eng. Chem.*, **4**, 493, 1912; S. J. Johnstone, *Journ. Soc. Chem. Ind.*, **33**, 55, 1914; R. B. Moore, *U.S.A. Bur. Mines Bull.*, **212**, 320, 1923; P. Wenger and P. Christin, *Ann. Chim. anal. Chim. appl.*, **4**, 231, 1922; G. Chesnau, *Compt. rend.*, **153**, 429, 1911; F. Hecht and E. Kroupa, *Zeit. anal. Chem.*, **102**, 81, 1935; H. H. Helmick, *Journ. Amer. Chem. Soc.*, **43**, 2003, 1921; C. James and A. J. Grant, *ib.*, **38**, 41, 1916; A. M. Ismail and H. F. Harwood, *Analyst*, **62**, 185, 1937.

[2] G. von Knorre, *Zeit. angew. Chem.*, **10**, 685, 717, 1897; *Ber.*, **33**, 1924, 1900; A. Job, *Compt. rend.*, **128**, 101, 180, 1899; E. Hintz, *Zeit. anal. Chem.*, **37**, 94, 504, 1898; *Chem. News*, **79**, 25, 41, 1899; G. P. Drossbach, *Ber.*, **29**, 2452, 1896; **35**, 2830, 1902; A. Waegner and A. Müller, *ib.*, **36**, 282, 1903; F. J. Metzger, *Journ. Amer. Chem. Soc.*, **31**, 523, 1909; L. Schneider, *Dingler's Journ.*, **269**, 224, 1888; W. Muthmann and L. Weiss, *Liebig's Ann.*, **331**, 1, 1904; T. Lindeman and M. Hafstad, *Zeit. anal. Chem.*, **70**, 433, 1927; G. Autié, *Bull. Soc. chim.*, (4), **41**, 1535, 1927; H. N. Furman, *Journ. Amer. Chem. Soc.*, **50**, 755, 1928. For the determination of cerium by the titration of cerous salts in neutral solution with permanganate, see R. J. Meyer and A. Schweitzer, *Zeit. anorg. Chem.*, **54**, 104, 1907; V. Lenher and C. C. Meloche, *Journ. Amer. Chem. Soc.*, **38**, 66, 1916; L. A. Congdon and E. L. Ray, *Chem. News*, **128**, 233, 1924; B. Brauner, *ib.*, **71**, 285, 1895; G. Autié, *Bull. Soc. chim.*, (4), **41**, 1535, 1927; F. Stolba, *Chem. Centr.*, (3), 595, 1879; G. A. Barbieri, *Atti. R. Accad. Lincei*, (5), **25**, i, 37, 1916. For other volumetric methods, see J. Šterna-Boehm and V. Matula, *Rec. Trav. chim.*, **44**, 400, 1925; R. Lessing, *Zeit. anal. Chem.*, **71**, 161, 1927; R. Lang and J. Zwěrina, *ib.*, **91**, 5, 1932.

solutions which have been exposed to the air for some time, the reduction may take a quarter of an hour. Hence, if an old solution be titrated with permanganate within a quarter of an hour after adding the hydrogen peroxide, the results will be low. When the reduction is completed, the total permanganate consumed with both old and new solutions is the same. If an old solution be boiled for a few minutes with dilute sulphuric acid and cooled, before adding the hydrogen peroxide, the rate of the reduction is accelerated.

Oxidation of Cerous to Ceric Salts.— Acidify the solution in an Erlenmeyer's flask with dilute sulphuric acid,[1] and add 2 grms. of ammonium persulphate [2] to the cold solution. Heat the solution to boiling for a couple of minutes. Cool to between 40° and 60° by dipping the flask containing the solution in cold water. Add half a gram of ammonium persulphate,[3] heat the solution to boiling for about 5 minutes; cool, add another half gram of the persulphate and boil 15 minutes, adding more dilute sulphuric acid towards the end of the boiling in order to decompose all the ammonium persulphate. Cool.[4]

The Titration.— Acidify the solution with sulphuric acid, and then add an excess of hydrogen peroxide.[5] The hydrogen peroxide is added from a burette until the solution is decolorised, and then a small excess of the peroxide is run into the solution. When the reaction between the yellow ceric salt and the hydrogen peroxide is over, titrate the residual hydrogen peroxide with potassium permanganate until the solution acquires a rose colour which persists for at least half a minute.[6]

Calculation.— Suppose that (1) 25 c.c. of the hydrogen peroxide solution react with 29·8 c.c. of a solution of potassium permanganate, containing 1·934 grms. of the salt per litre,[7] and (2) after adding 25 c.c. of the hydrogen peroxide solution to the solution of ceric cerium, 12·2 c.c. of permanganate are needed to react with the excess of hydrogen peroxide. The ceric salts in the solution thus correspond with 29·8 − 12·2 = 17·6 c.c. of the permanganate. The reaction between the permanganate and the hydrogen peroxide is represented by the equation—

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

and that between ceric sulphate and hydrogen peroxide by—

$$2Ce(SO_4)_2 + H_2O_2 = Ce_2(SO_4)_3 + H_2SO_4 + O_2$$

Hence 2 grm.-molecules or 316·05 grms. of potassium permanganate correspond with 10 grm.-atoms or 10 × 140·13 grms. of cerium, that is, 10 × 172·13 grms. of

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[1] According to T. Lindeman and M. Hafstad (*Zeit. anal. Chem.*, **70**, 433, 1927) the solution should not contain more than 4·6 grms. nor less than 2·7 grms. of sulphuric acid per 100 c.c. and, in the presence of other metals, at least 5 grms. of magnesium as sulphate must be added per gram of cerium to prevent spontaneous reduction of ceric sulphate. N. H. Furman (*Journ. Amer. Chem. Soc.*, **50**, 755, 1928) failed to confirm some of these conclusions.

[2] H. H. Willard and P. Young (*Journ. Amer. Chem. Soc.*, **50**, 1379, 1928) use silver nitrate to accelerate catalytically the oxidation. The ceric salt is then titrated potentiometrically with standard ferrous sulphate. For other potentiometric methods of determining cerium, see O. Tomiček, *Rec. Trav. chim.*, **44**, 410, 1925; I. A. Atanasiu, *Journ. Chim. Phys.*, **23**, 501, 1926; *Bul. Chim. Soc. Române Stiin.*, **30**, 51, 1928; K. Someya, *Zeit. anorg. Chem.*, **168**, 56, 1927; **184**, 428, 1929; G. Autié, *Bull. Soc. chim.*, (4), **41**, 1535, 1927.

[3] 3 grms. of ammonium persulphate suffice for the oxidation of 0·2 to 0·3 grm. cerium.

[4] If all the cerium is initially present as ceric sulphate, this preliminary oxidation is unnecessary.
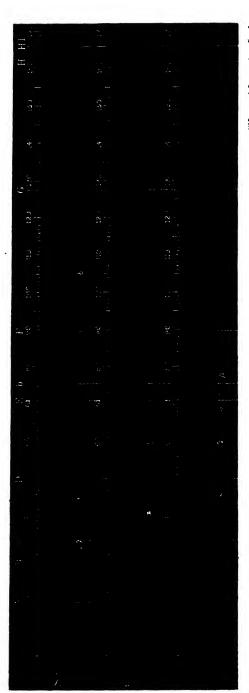
[5] G. Autié (*l.c.*) recommends that the hydrogen peroxide should be in concentrated nitric acid solution, otherwise errors may arise owing to the precipitation of ceric hydroxide.

[6] The slow decomposition of potassium permanganate by cerous sulphate does not interfere with the recognition of the end-point in the permanganate titration.

[7] The permanganate solution should contain not more than about 2 grms. of the salt per litre.

CeO_2. Consequently 17·6 c.c. of the permanganate solution correspond with $(17·6 \times 0·001934 \times 10 \times 172·13)/316·05 = 0·1854$ grm. CeO_2 in the solution. Phosphoric and titanic acids disturb the action. The results are very fair if the above directions be carefully followed.[1]

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[1] For the separation of cerium as iodate, see P. H. M. P. Brinton and C. James, *Journ. Amer. Chem. Soc.*, **41**, 1080, 1919; as fluoride, K. Swoboda and R. Horny, *Zeit. anal. Chem.*, **67**, 386, 1926; as phosphate, J. W. Neckers and H. C. Kremers, *Journ. Amer. Chem. Soc.*, **50**, 955, 1928. For the determination of cerium in lead alloys, see B. S. Evans, *Analyst*, **58**, 450, 1933.

PLATE I.

Chemical Analysis, J. W. Mellor, D.Sc., London, Charles Griffin & Co., Ltd

SPECTRA OF METALS OF ALKALINE EARTHS (WITH FRAUNHOFER'S LINES OF SOLAR SPECTRUM AS STANDARDS OF REFERENCE

CHAPTER XXXVI.

SPECIAL METHODS FOR THE DETERMINATION OF BARIUM, STRONTIUM, CALCIUM AND MAGNESIUM.

§ 283. The Influence of Barium and Strontium on the Calcium and Magnesium Precipitates.

THE spectroscopic test for barium and strontium is generally applied to the ignited calcium oxalate precipitate when these elements are sought in a silicate analysis.[1] These elements have characteristic spectra (Plate I.). It is assumed that sufficient barium and strontium will be precipitated with the

[1] A small direct-vision spectroscope with a scale is a very convenient adjunct for deciding if certain precipitates are properly washed. Fig. 118 illustrates the method of using the
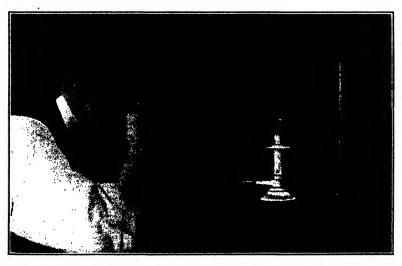
FIG. 118.—Spectroscopic Test.

spectroscope. The loop of platinum wire in the Bunsen flame (porcelain burner) has been dipped in a drop of the solution under investigation. F. von Kobell (*Journ. prakt. Chem.*, (2), 3, 176, 1871) applies the spectroscope test to silicates by placing the powdered mineral, moistened with hydrochloric acid, on a piece of platinum foil, perforated with small holes and bent in the form of a trough. The arrangement is held in the flame by a pair of platinum-tipped tongs. The spectra of barium, strontium and calcium are illustrated in Plate I. The spectroscopic method will detect $\frac{1}{1000}$ mgrm. of baryta; $\frac{6}{100,000}$ mgrm. of strontia; and $\frac{6}{100,000}$ mgrm. of lime (Bunsen). Strontium, if present as phosphate, may elude spectrographic examination—J. Meunier, *Compt. rend.*, 182, 1160, 1926.

lime to reveal their presence, in spite of the fact that barium and strontium oxalates are more soluble than the corresponding calcium oxalate.[1] Hillebrand[2] says that "this assumption, in the case of strontium, is well founded, but it may be entirely fallacious in the case of barium." For instance, a mineral containing 0·76 per cent. of barium gave no indication of barium under the conditions of the test. This is due to the solvent action of ammonium chloride upon the barium oxalate. In a series of experiments with artificial mixtures of calcium with barium and with strontium, it was found that strontium and barium are but very incompletely precipitated by the addition of a slight excess of ammonium oxalate, but a greater proportion is precipitated when a large excess of ammonium oxalate is used. With traces of strontium in the presence of a large excess of calcium, most of the strontium is precipitated with the calcium; but this action was not noticed with barium, a considerable proportion of the barium escaping precipitation with the calcium, and therefore being sought in the filtrate. With a double precipitation of the lime, much of the strontium will be associated with the lime but practically no barium, provided the amount of barium does not exceed 0·2 or 0·3 per cent. If more than this amount of barium be present, the precipitation by ammonium oxalate can be repeated a third and fourth time, or the strontium and barium can be recovered from the final lime precipitate and then separated by the process described below.

If barium be present, it may also contaminate the ammonium magnesium phosphate precipitate as barium phosphate. In that case, the barium must be removed[3] before precipitating the magnesium ammonium phosphate. Evaporate the filtrate from the calcium oxalate to dryness; ignite the residue in a porcelain dish to drive off the ammonium salts; take up the residue with water acidified with hydrochloric acid; add three drops of sulphuric acid; let the mixture stand about 12 hours. If a precipitate forms, filter and treat the precipitated barium sulphate as described below. Determine the magnesia in the filtrate as indicated on page 208.

§ 284. The Separation of Calcium from Strontium and Barium — Stromeyer and Rose's Process.

If strontium be present, most of it will be found associated with the lime. The separation of calcium and strontium is conveniently done by Stromeyer's process improved by Rose.[4] The mixed oxalates are ignited as usual and weighed as oxides.

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[1] For the solubility of barium oxalate, see E. Groschuff, *Ber.*, **34**, 3313, 1901; F. Kohlrausch, *Zeit. phys. Chem.*, **64**, 121, 1908. For strontium oxalate, see F. Kohlrausch, *l.c.*; H. Cantoni and D. Diotalevi, *Bull. Soc. chim.*, (3), **33**, 27, 1905.

[2] W. F. Hillebrand, *Journ. Amer. Chem. Soc.*, **16**, 81, 83, 1894; *Bull. U.S. Geol. Sur.*, **422**, 120, 1910; *Chem. News*, **69**, 142, 147, 1894; C. A. Peters, *Amer. Journ. Sci.*, (4), **12**, 216, 1901. For the determination of strontium as oxalate, see L. W. Winkler, *Zeit. angew. Chem.*, **31**, (1), 80, 83, 1918; K. N. Pochinok, *Journ. Applied Chem.* (*U.S.S.R.*), **5**, 1078, 1932; for barium as oxalate, B. N. Angelescu, *Bull. Soc. chim. România*, **5**, 12, 1923.

[3] R. Langley (*Amer. J. Science*, (4), **26**, 123, 1908) removes the barium by precipitation with sulphuric acid just after the separation of silica; redissolves the precipitate in concentrated sulphuric acid and reprecipitates it with water, in order to remove ferric and other sulphates.

[4] F. Stromeyer, *Gilbert's Ann.*, **54**, 245, 1816; H. Rose, *Pogg. Ann.*, **110**, 292, 1860; R. Fresenius, *Zeit. anal. Chem.*, **29**, 20, 143, 413, 1890; **30**, 18, 452, 583, 1891; **32**, 189, 1893; *Chem. News*, **68**, 213, 1893; J. L. M. van der Horn van der Bos, *Chem. Weekb.*, **8**, 5, 1911; S. P. L. Sorensen, *Zeit. anorg. Chem.*, **11**, 305, 1896; W. Noll, *ib.*, **199**, 193, 1931; O. B. Winter, *Journ. Ind. Eng. Chem.*, **8**, 603, 1916; P. E. Browning (*Amer. J. Science*, (3), **43**, 50,

Calcium.—The oxides are dissolved in dilute nitric acid (1 : 5) in a small 25 c.c. stoppered flask,[1] and the solution evaporated to dryness at 150° to 160° in a stream of dry air in an attachment resembling that used for lithium (fig. 121, page 603). Treat the dry mass in the stoppered flask with about 10 times its weight of a mixture of equal volumes of absolute ether and absolute alcohol, in which the barium and strontium nitrates are but sparingly soluble,[2] while calcium nitrate is readily soluble. Let the flask stand about 12 hours, with occasional shaking. Filter through a small (5·5 cm.) filter-paper moistened with a few drops of the ether-alcohol mixture. Wash with the mixture of ether and alcohol until a drop of the washing gives no residue when evaporated to dryness on a clean piece of platinum foil [3] — about six washings usually suffice. Evaporate the filtrate to dryness. Dissolve the calcium nitrate in water and precipitate the calcium as oxalate in the usual way (page 202).

Strontium.—The strontium can be determined by difference, or directly as follows. Dissolve the residue on the filter-paper in dilute nitric acid; collect the washings in a 50 c.c. beaker and add sulphuric acid (1 : 2) almost equal in volume to the liquid in the beaker. In about 12 hours, filter off the precipitate, ignite [4] and weigh as strontium sulphate—$SrSO_4$. The weight of strontium sulphate so obtained, multiplied by 0·5641, gives the corresponding amount of strontia—SrO.

Barium.—If barium be present in the calcium oxalate precipitate, it will also be found with the strontium sulphate. The barium and strontium can be separated by the chromate process described below.[5] If barium and strontium are to be determined, it is advisable to combine the filtrates from the calcium oxalate with the strontium and barium separated from the calcium itself,

1892; (3), 44, 462, 1892; *Chem. News*, 67, 45, 53, 1893; 65, 271, 282, 1892; 66, 3, 1892) recommends amyl alcohol in place of the mixture of alcohol and ether employed in Stromeyer and Rose's process; L. Moser and L. Machiedo (*Chem. Ztg.*, 35, 337, 1911) say that amyl alcohol offers no advantages over the ether-alcohol mixture. L. Szebellédy (*Zeit. anal. Chem.*, 70, 39, 1927; *Magyar Chem. Fol.*, 35, 59, 63, 1929; *Chem. Zentr.*, (2), 274, 1930) extracts first with absolute alcohol and then with isobutyl alcohol.

[1] A weighing bottle like fig. 1, *b*, may be used for this purpose.

[2] About 0·0017 per cent. of strontium nitrate.

[3] Take care that no flame is near the ether-alcohol. The mixture is very inflammable.

[4] If the ignition temperature be too high, some of the sulphate may decompose. For the loss on heating strontium sulphate, see M. Darmstadt, *Zeit. anal. Chem.*, 6, 376, 1867; A. Mitscherlich, *Journ. prakt. Chem.*, (1), 83, 485, 1861; J. Boussingault, *Compt. rend.*, 64, 1159, 1867.

[5] A rough separation of barium from strontium can be effected by digesting the mixed sulphates in a cold concentrated solution of ammonium carbonate. Wash the mixed sulphates into a funnel with a stopcock and fill the funnel with the solution of ammonium carbonate. Let the whole stand 12 hours. The strontium sulphate is converted into strontium carbonate, while the barium sulphate is but slightly affected. The precipitate is then washed with hot water, dilute hydrochloric acid and finally with water. Ignite and weigh as barium sulphate. The strontium is determined by neutralising the filtrate with ammonia, precipitation with ammonium carbonate, converting the ignited strontia into sulphate and weighing as strontium sulphate. If the barium predominates, an appreciable quantity of strontium sulphate escapes decomposition; and when the strontium is in excess, an appreciable quantity of barium sulphate will be decomposed. R. Fresenius, *Zeit. anal. Chem.*, 29, 20, 1890; S. G. Rawson, *Journ. Soc. Chem. Ind.*, 16, 113, 1897; H. Rose, *Pogg. Ann.*, 95, 286, 299, 427, 1855. See P. Schweitzer (*Contrib. Lab. State Univ.*, 1, 1876; *Proc. Amer. Assoc.*, 187, 1877; J. L. Morgan, *Journ. Amer. Chem. Soc.*, 21, 522, 1899; F. W. Küster, *Zeit. anorg. Chem.*, 22, 161, 1899) for the theory of the reaction. For the separation of strontium and barium through the differential solubility of their bromides in amyl and isobutyl alcohols, see respectively P. E. Browning, *Amer. Journ. Science*, (3), 44, 459, 1892, and L. Szebellédy, *Zeit. anal. Chem.*, 78, 198, 1929. For the separation as silicofluorides, see R. Fresenius, *Zeit. anal. Chem.*, 29, 143, 1890; R. Leo, *Monats.*, 43, 567, 1923; as chlorides, F. A. Gooch and M. A. Soderman, *Amer. Journ. Sci.*, (4), 46, 538, 1918.

and then apply the chromate process to the combined filtrates. But there are so many leakages of barium and other sources of error in the analysis that it is best to determine the barium on a separate sample, either by the hydrofluoric decomposition process or by the process of decomposition indicated on page 581.

§ 285. The Separation of Barium from Strontium and Calcium—Chromate Process.

The separation of barium, strontium and calcium can be conveniently effected by (1) removing the calcium as nitrate by Stromeyer and Rose's process, and then separating the barium and strontium by the chromate process; or (2) separating barium from the neutral solution of the mixed chlorides by the chromate process, precipitating the calcium and strontium as carbonates by means of ammonium or sodium carbonate and, after transforming the carbonates into nitrates, using Stromeyer and Rose's process for the calcium and strontium.

The transformation of the mixed carbonates or oxides into nitrates offers no difficulty, but the chlorides are not completely converted into nitrates by repeated evaporation with nitric acid.[1] It is best to precipitate the carbonates with ammonium or sodium carbonate and digest the carbonates with as little nitric acid as possible in a small flask, taking care to avoid loss by spurting.

First Precipitation of Barium Chromate.[2]—Evaporate the mixed nitrates to dryness and dissolve the mixture in water. To the solution add an excess, say 10 c.c., of a solution of ammonium acetate [3]; heat the solution to boiling and gradually add, with constant agitation, 5 c.c. of ammonium dichromate solution.[4] Let the precipitate settle and, when the solution is cold, decant the clear liquid through a filter-paper and wash the precipitate by decantation with a dilute solution of ammonium acetate [5] until the filtrate is no longer perceptibly coloured. About 100 c.c. of liquid will be needed for the washing. Some strontium, if present, may be carried down with the barium chromate, hence the precipitate is dissolved in dilute acid and reprecipitated.

Second Precipitation of Barium Chromate.—Place a beaker under the funnel and dissolve the precipitate on the filter-paper by running warm dilute nitric acid (1 : 5) through the filter-paper, collecting the "runnings" in the vessel in which the precipitation was first made. Wash the paper. Add ammonia to the solution until the precipitate which forms no longer redissolves when the solution is agitated. Add, with constant agitation, 10 c.c. of the concentrated

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[1] If magnesium be present, it too will be precipitated, and the chromium must later on be separated from the filtrate before the magnesium can be precipitated as phosphate. The chromium is separated by reducing the chromate as described on page 534, and precipitating the chromium as hydroxide by the addition of ammonia.

[2] The properties of barium chromate were discussed on page 532. It might be added that barium chromate is not soluble in water containing acetic acid when so much ammonium chromate is present that the solution contains only alkali acetate and dichromate (H. N. Morse, *Amer. Chem. Journ.*, 2, 176, 1880).

[3] AMMONIUM ACETATE.—Neutralise an aqueous solution of 300 grms. of "pure" commercial ammonium acetate with ammonia and make the solution up to a litre. See R. Reik (*Monats.*, 23, 1033, 1902), A. Mittasch (*Zeit. anal. Chem.*, 42, 492, 1903), and L. H. Duschak (*Journ. Amer. Chem. Soc.*, 30, 1827, 1908) for the impurities in the commercial salt.

[4] AMMONIUM DICHROMATE SOLUTION.—Dissolve 100 grms. of the salt, free from sulphates or sulphuric acid, in a litre of water.

[5] Made by diluting 20 c.c. of the above concentrated solution of ammonium acetate to a litre.

solution of ammonium acetate; heat the solution to boiling. Let the solution settle till cold and then filter through a weighed Gooch crucible packed with asbestos felt. Wash the precipitate as before. Dry, ignite and weigh as described on page 533.[1] The weight of the barium chromate multiplied by 0·6053 gives the corresponding amount of barium oxide—BaO.

Determination of Strontium.—The strontium may be precipitated from the combined filtrates by the addition of ammonia and ammonium carbonate after the solution has been concentrated in the presence of an excess of nitric acid. The precipitated strontium carbonate may contain a little chromic acid. This is removed either by dissolving the precipitate in hydrochloric acid and precipitating the strontium as sulphate (page 579) in the presence of alcohol, if strontium alone and no calcium be present; or, by the application of the ether-alcohol process (page 579) in the event of both strontium and calcium being present.[2]

Kämmerer[3] first used potassium chromate for the qualitative precipitation of barium in the presence of calcium and strontium from solutions containing acetic acid and ammonium acetate; Frerichs applied the reaction quantitatively and Russmann showed that very fair results could be obtained with the process. Fresenius investigated the conditions which favoured success and failure, and Skrabal and Neustadtl have developed the process in its present form, whereby a satisfactory separation can be made.

§ 286. The Determination of Barium in Insoluble Silicates.

Decomposition by Fusion with Sodium Carbonate.—It is not advisable generally to separate barium quantitatively from a solution which has previously been used for the determination of the members of the hydrogen sulphide, ammonia and ammonium sulphide groups, because of the leakage or loss of barium entailed during the separations. In the hydrogen sulphide group the main loss is due to the reduction of ferric chloride by hydrogen sulphide and oxidation of the sulphide to sulphate,[4] which means that barium sulphate will be precipitated. In a solution containing 100 mgrms. of barium

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[1] Simply drying at 110° is not sufficient; the precipitate must be gently ignited (see page 533).

[2] For the simultaneous determination of calcium and strontium by indirect methods, see R. L. y Gamboa, *Anal. Fis. Quim.*, **10**, 389, 1912; S. D. Averitt, *Journ. Ind. Eng. Chem.*, **9**, 584, 1917; O. Arnd and E. A. Hafner, *Biochem. Ztg.*, **174**, 182, 1926.

[3] H. Kämmerer, *Zeit. anal. Chem.*, **12**, 375, 1873; J. Meschezerski, *ib.*, **21**, 399, 1882; E. Fleischer, *ib.*, **9**, 97, 1870; R. Fresenius, *ib.*, **29**, 20, 143, 413, 1890; **30**, 18, 452, 583, 1891; **32**, 183, 312, 1893; *Chem. News*, **67**, 213, 1893; A. Skrabal and L. Neustadtl, *Zeit. anal. Chem.*, **44**, 742, 1905; W. Fresenius and F. Ruppert, *ib.*, **30**, 672, 1891; A. Russmann, *ib.*, **29**, 447, 1890; *Chem. News*, **63**, 13, 44, 1891; P. Schweitzer, *Proc. Amer. Assoc.*, **37**, 1877; H. Baubigny, *Bull. Soc. chim.*, (3), **13**, 326, 1895; H. Baubigny, *ib.*, (4), **1**, 55, 1907; H. Caron and M. Raquet, *ib.*, (3), **35**, 1061, 1906; F. Frerichs, *Ber.*, **7**, 800, 956, 1874; H. Robin, *Ann. Chim. anal.*, **18**, 445, 1903; B. Kahan, *Analyst*, **33**, 12, 1908; J. L. M. van der Horn van der Bos, *Chem. Weekblad*, **8**, 5, 1911; **9**, 1002, 1912; **10**, 665, 1913; H. B. Vickery, *Trans. Nova Scotian Inst. Science*, **14**, 30, 1914; A. C. Peterson, *Journ. Amer. Chem. Soc.*, **37**, 2346, 1915; L. Szebellédy, *Chem. Zentr.*, (2), 770, 1929; *Magyar Chem. Fol.*, **35**, 77, 1929; R. Strebinger, *Mikrochem.*, **7**, 100, 1929; E. Beyne, *Chimiste*, **3**, 256, 1912—Sr in zinc blendes. The barium can be determined volumetrically by dissolving the precipitated chromate in dilute hydrochloric acid, adding potassium iodide and titrating the liberated iodine with thiosulphate—I. M. Kolthoff, *Pharm. Weekb.*, **57**, 972, 1920; S. R. Goday, *Bol. Farm. Mil.*, **10**, 202, 1932.

[4] A. A. Noyes and W. C. Bray (*Journ. Amer. Chem. Soc.*, **29**, 137, 1907) state that the presence of 500 mgrms. of $FeCl_3$ in solution leads to the precipitation of as much as 20 mgrms. of barium as sulphate in the hydrogen sulphide group.

in 100 c.c., Curtman and Frankel found [1] that 1·4 mgrms. of barium are lost in the hydrogen sulphide group, owing to the oxidation of hydrogen sulphide to sulphuric acid; 14·0 mgrms. are lost by the action of ferric chloride on hydrogen sulphide; 14·7 mgrms. are lost due to the absorption of carbon dioxide by the ammonia used for the ammonia precipitation; and between 2 and 3 mgrms. are lost in the precipitation by ammonium sulphide. Losses of barium may also occur owing to the presence of traces of sulphates in the reagents and also to the retarding influence of ammonium salts on the precipitation of barium sulphate or carbonate. Hence it is best to determine barium on a special sample, and not on the sample used for the main analysis.

When a silicate contains barium, the silicate is fused with sodium carbonate, the resulting cake is digested with water and the residue treated with sulphuric acid. The insoluble portion contains the barium, silica and possibly some calcium and strontium, if present, while aluminium, iron, zirconium, etc., pass into the acid filtrate.

To determine the total barium, ignite the filter-paper containing the insoluble residue. Fuse with a gram of sodium carbonate for 10 to 15 minutes. Dissolve the mass in warm water, filter and wash thoroughly. Place a 250 c.c. beaker below the funnel and dissolve the precipitate off the paper in dilute hydrochloric acid. Wash the filter-paper well. Nearly neutralise the filtrate with sodium carbonate and make the solution up to, say, 150 c.c. so that the dilution is sufficiently great to prevent the precipitation of calcium sulphate later on. Precipitate the barium by the addition of a hot solution of dilute sulphuric acid (3 in 50 by volume) to the boiling solution. The addition is made gradually, with constant stirring. The reasons will appear from the discussion on page 703. Wash by decantation [2]; collect the precipitate in a small filter-paper and ignite the barium sulphate, with the precautions indicated on page 700. The weight of the barium sulphate multiplied by 0·6570 gives the corresponding amount of barium oxide—BaO.

Purification from Calcium.—If much calcium be present, the ignition should be made in a platinum crucible and the ignited precipitate fused with sodium carbonate. The resulting cake is treated with water and acidified with acetic acid, which is added drop by drop. The barium is precipitated by the addition of sulphuric acid as before.[3]

Hydrofluoric Acid Decomposition.—The total barium is conveniently determined in silicates [4] by treating 2 grms. of the finely powdered, dry (110°) silicate with 10 c.c. of sulphuric acid (1 : 4) and 5 c.c. of hydrofluoric acid in a large platinum crucible. Evaporate the solution on a water bath, add more hydrofluoric acid and repeat the evaporation. If no sandy grains can be detected with a platinum spatula, further treatment with the hydrofluoric acid is not necessary. Heat the mixture on a sand bath until most of the sulphuric acid has been driven off. Let the crucible cool and wash its contents into, say, 25 c.c. of water. The precipitate of barium sulphate will probably be free from calcium, but a little strontium may be present. Filter off the barium sulphate. Ignite in a platinum crucible; cool.

Purification from Calcium and Strontium.—The strontium and calcium can be removed by dissolving the barium sulphate in concentrated sulphuric acid

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[1] L. J. Curtman and E. Frankel, *Journ. Amer. Chem. Soc.*, 33, 724, 1911.

[2] The filtrate contains some silica, titanium, iron, aluminium, columbium, tantalum and tin, if these elements be present.

[3] Silica is not precipitated with barium sulphate from dilute solutions of sodium silicate.

[4] With glazes, lead sulphate may be present. This can be removed by digestion with ammonium acetate as described on page 325.

and again pouring the solution into water. If the amount of barium sulphate be less than about 0·002 grm., there is no need to purify the salt further.[1] Ignite the precipitated barium sulphate in a platinum crucible and weigh as barium sulphate.

§ 287. The Complete Analysis of Limestones and Gault Clays.

Limestones, gault clays, marls, dolomite, magnesite and similar carbonate rocks may be analysed from several different points of view; and, in consequence, a more or less incomplete analysis may serve all requirements. Some abbreviated methods will be described later.

Dissolution of the Sample.—A gram of the powdered and dried material is digested in a 100 c.c. beaker with 20 c.c. of water, 2 c.c. of concentrated hydrochloric acid and 2 drops of nitric acid. The acids are added slowly and the beaker is kept covered by a clock-glass with its convex side downwards, so as to avoid loss during the effervescence. When effervescence has ceased, heat the solution to its boiling-point on a hot plate, so as to drive off the carbon dioxide. Rinse the clock-glass with water. Filter the solution into an evaporating basin and wash the residue with water. Ignite the insoluble residue in a platinum crucible[2] and fuse it up with a little sodium carbonate. Remove the fused mass with water and dilute hydrochloric acid: keep the crucible covered during the action to avoid loss by spurting. Add the solution to the main solution.

If the limestone does not contain much more than about 5 per cent. alumina and ferric oxide, and 15 per cent. of silica, strong ignition over a blast[3] in a covered platinum crucible will frequently give a powder wholly soluble in hydrochloric acid (1 : 1), except, possibly, a little flocculent silica which does not matter. If too much siliceous matter be present to render this treatment successful, as is sometimes the case with siliceous limestones, magnesian limestones, cement rocks and highly calcareous marls, Meade[4] recommends igniting the limestone with just less than its own weight of sodium carbonate. The sintered, not fused, mass is then easily broken down by hydrochloric acid (1 : 1).

Determination of Silica, Alumina, Titanium, etc.—Evaporate[5] the combined filtrates to dryness for silica (page 147); determine the alumina, titanium, iron, phosphorus,[6] lime,[7] magnesia and manganese[3] as described for clays

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[1] If zirconium be present, it will be associated with the barium sulphate, and it must be removed as indicated on page 582.

[2] The insoluble residue is sometimes reported as such, or as "siliceous minerals," "clay and sand," etc. As a matter of fact, the term "insoluble residue" is more or less ambiguous, since the attack on the siliceous minerals is dependent on the strength of the acid and on the state of subdivision of the powder. The finer the sample is ground, the less the "insoluble residue."

[3] T. Engelbach, *Liebig's Ann.*, 123, 260, 1862.

[4] R. K. Meade, *Portland Cement*, Easton, Pa., 254, 1906.

[5] The evaporation is more rapid than with clays because of the absence of large amounts of alkali chlorides and a smaller volume of liquid is used for the dissolution of the fused cake.

[6] Phosphatic limestones may have less alumina than is needed to combine with the phosphorus and in that case some calcium phosphate will be precipitated with the aluminium and iron phosphates. Some, therefore, add a weighed quantity of a ferric salt to the solution before adding the ammonia, and afterwards deduct the amount of iron added from the ferric oxide obtained later—compare page 687.

[7] In the case of magnesites where but little calcium and much magnesium is present, the oxalate process for lime is not suitable (F. Hundeshagen, *Zeit. öffent. Chem.*, 15, 85, 1907). It is best to treat the filtrate—occupying, say, 30 c.c.—from the silica with 4 grms. of sodium sulphate and 40 c.c. of 90 per cent. alcohol. After standing about five hours at 17°–20° in

(pages 157 *et seq.*). The carbon dioxide (page 624), water (page 642) and the alkalies are determined on separate samples.[1]

Chlorine and Fluorine.—For the chlorine, digest, say, 10 grms. with water and nitric acid at a gentle heat. Filter and proceed by the method of page 746. For the fluorine, digest 10 grms. of the dry powdered sample in acetic acid,[2] without boiling or filtering, until the magnesium and calcium carbonates are decomposed. Evaporate the solution to dryness to expel the excess of acetic acid, add a slight excess of sodium carbonate and extract the residue with water. The precipitate of calcium fluoride, carbonate and insoluble residue is treated by the process of page 725.

Determination of Sulphur. Sulphides as well as sulphates are often present in limestones and calcareous clays. To determine the "sulphate or soluble sulphur," digest, say, 2 grms. of the powdered sample in a large porcelain basin with 40 c.c. of water and 5 c.c. of concentrated hydrochloric acid. Evaporate the solution to dryness. Boil the residue with water, filter and wash.[3] Precipitate the sulphuric acid in the filtrate as barium sulphate by the method of page 703. The weight of barium sulphate so obtained, multiplied by 0·3430, represents the corresponding amount of sulphur trioxide —SO_3; and when multiplied by 0·58324, the corresponding amount of calcium sulphate.

To get the "total sulphur," place 2 grms. of the powdered sample in a porcelain evaporating basin and cover the mass with bromine water. Decompose the carbonates by adding 25–30 c.c. of hydrochloric acid, in small

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a covered vessel, filter the solution and wash the precipitated calcium sulphate with 75 per cent. alcohol. In order to free the precipitate completely from magnesia, redissolve the sulphate in hot dilute hydrochloric acid and precipitate the lime as usual by the oxalate process. The combined filtrates from the calcium sulphate and oxalate are evaporated to drive off the alcohol and the iron is oxidised with hydrogen peroxide. The aluminium and ferric hydroxides are precipitated by adding ammonia and the magnesia is determined in the filtrate in the usual way. W. F. Hillebrand and G. E. F. Lundell (*Applied Inorganic Analysis*, New York, 488, 1929) recommend the following process. The calcium is precipitated as phosphate with the magnesium. The ignited and weighed precipitate of mixed phosphates is dissolved in not more than 0·5 c.c. excess of dilute sulphuric acid and to the solution 100 c.c. of 75 per cent. alcohol are added for every 0·3 grm. of mixed phosphates originally present. The mixture is stood overnight, the calcium sulphate is filtered off, washed with 75 per cent. alcohol, dissolved in dilute hydrochloric acid and the calcium reprecipitated as oxalate. In this procedure the phosphate precipitate must be ignited in a platinum crucible and not a Gooch crucible.

[8] The manganese will be found in the filtrate from the ammonia precipitate or it may be precipitated with the alumina by adding bromine as indicated on page 157. Copper, lead, zinc, nickel (sulphides or carbonates), rare earths, chromium and vanadium must be determined on large quantities of the sample—say 50–500 grms.

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[1] As a rule, in Smith's process, about half as much calcium carbonate is needed for limestones and the more calcareous clays as is indicated in the standard directions (page 214). The precipitated calcium carbonate is much more effective in the work of decomposition than the native crystalline carbonate. For the distinction between precipitated calcium carbonate, limestone and chalk, see J. Ranedo, *Anales Soc. Españ. Fis. Quim.* (*Technica*), **27**, 168, 1929. If no precipitated carbonate be used, the results, with Smith's process, are usually rather low. T. Engelbach (*Liebig's Ann.*, **123**, 260, 1862) uses a modification of Berzelius' process for the alkalies in the "soluble" portion of limestones. Ignite the powdered mineral strongly over a blast, boil with a little water, filter, neutralise the solution with hydrochloric acid. Treat the solution with ammonia and ammonium carbonate (page 217).

[2] G. Jenzsch, *Pogg. Ann.*, **96**, 145, 1855.

[3] If phosphorus is to be determined, it is sometimes advisable to take double the amount of the sample for the operation just described and make the filtrate up to 100 c.c. Take 50 c.c. for the sulphur determination and to the other 50 c.c. add 5 c.c. of nitric acid and determine the phosphorus by Woy's process (page 672).

quantities at a time, to the cold solution. The "sulphide sulphur" is liberated as hydrogen sulphide and immediately oxidised by the bromine water. If the acid be added gradually and the bromine water be in excess, there will be no appreciable loss of sulphide. The solution is evaporated to dryness, filtered and the sulphuric acid in the filtrate precipitated as barium sulphate, as indicated on page 703. The difference between the weights of barium sulphate obtained with and without the bromine water, multiplied by 0·13735, represents the corresponding amount of "sulphide sulphur." [1]

Example.—Suppose the following results have been obtained:—

Barium sulphate (with bromine)	.	.	.	.	0·0341 grm.
Barium sulphate (without bromine)	.	.	.	.	0·0251 grm.
Barium sulphate from sulphide	.	.	.	.	0·0090 grm.
Sulphide sulphur (0·0090 × 0·13735)	.	.	.	.	0·0012 grm.
Sulphur trioxide (0·0251 × 0·3430)	.	.	.	.	0·0086 grm.
Calcium sulphate (0·0251 × 0·58324)	.	.	.	.	0·0146 grm.

Sometimes the total sulphur is determined by one of the methods described on pages 704 et seq. Or the powdered sample can be fused with sodium carbonate and sodium nitrite (page 510).[2] Extract the mass with water. Acidify the filtrate with hydrochloric acid, guarding against loss by spurting, and evaporate to dryness. Moisten the residue with hydrochloric acid, filter, wash and determine the sulphates in the filtrate by the method of page 703.

Organic Matter is found in nearly all limestone rocks. Schaffgotsch's process for the determination of organic matter is to fuse, say, 5 grms. of borax glass in a platinum crucible over a Bunsen burner [3] until the weight of the crucible and contents is constant.[4] Place 1 grm. of the sample on the borax, put the lid of the crucible in position and fuse over the Bunsen burner. Do not remove the lid until the contents are fused, otherwise loss by decrepitation may occur. When the evolution of gas has ceased, cool in a desiccator and weigh. Again ignite, cool and weigh. When the weight is constant, the loss in weight of the crucible and its contents represents the carbon dioxide, water and organic matter. If the carbon dioxide and water have been previously determined, the amount of organic matter follows by difference.

Petzholdt [5] recommends the following process:—Dissolve 20 grms. of the

[1] Pyrite—FeS$_2$—is the commonest sulphide in limestone rocks. See G. Ortner, *Zeit. anal. Chem.*, 106, 28, 1936. Some of the sulphur may come from the organic matter.

[2] A. Petzholdt, *Journ. prakt. Chem.*, (1), 63, 194, 1854; J. Roth, *ib.*, (1), 58, 84, 1853; J. J. Ebelmen, *Compt. rend.*, 33, 881, 1851; H. St C. Deville, *ib.*, 37, 1001, 1853.

[3] Note, if a blast be used initially, the crucible and contents must be afterwards brought to constant weight over the Bunsen burner. Borax glass can be kept in a state of fusion some 15–30 minutes without appreciable volatilisation, but there is a decided loss after a few minutes' blasting (page 651). R. Fresenius, *Zeit. anal. Chem.*, 1, 65, 1862; A. Mitscherlich, *Journ. prakt. Chem.*, (1), 83, 485, 1861.

[4] According to O. Lutz and A. Tschischikow (*Journ. Russ. Phys. Chem. Soc.*, 36, 1274, 1904), microcosmic salt may be used in place of borax. The salt is heated until ammonia and water have been expelled and the weight is constant. The advantage of microcosmic salt is: (1) it fuses more quickly; (2) is not so liable to loss by volatilisation. H. Rose (*Pogg. Ann.*, 116, 131, 686, 1862; *Zeit. anal. Chem.*, 1, 183, 1862) recommends potassium dichromate; W. Böttger (*Zeit. anal. Chem.*, 49, 487, 1910), sodium metaphosphate (see page 757); F. A. Gooch and S. B. Kuzirian (*Amer. J. Science*, (4), 31, 497, 1911), sodium paratungstate; and H. Rose (*Pogg. Ann.*, 116, 635, 1862; T. W. Richards and E. H. Archibald, *Proc. Amer. Acad.*, 38, 443, 1903), silica.

[5] A. Petzholdt (*Journ. prakt. Chem.*, (1), 63, 194, 1854) considers that 58 parts of carbon correspond with 100 parts of humus. If carbon and hydrogen are both determined by combustion, 4·5 parts of hydrogen correspond with every 58 parts of carbon. The remaining

sample in dilute hydrochloric acid and boil the solution carefully to expel carbon dioxide. Filter off any undissolved residue through ignited asbestos, wash well with water and dry. Transfer the asbestos to a porcelain boat and determine the carbon in the residue by combustion to carbon dioxide as given on page 631; or the carbon may be determined by the wet process (page 616).

§ 288. The Partial Analysis of Limestones, Dolomites, Magnesites, Marls and Cements.

A process which occupies about three hours may now be described. The abbreviated processes are not usually quite so exact as the preceding process, but they are quite accurate enough for many purposes, particularly when a great number of analyses of one type of carbonate rock have to be made rapidly.[1] See the remarks on pages 239 and 244.

1. *Silica.*—Cautiously add 5 c.c. of concentrated hydrochloric acid to a gram of the powdered sample, keeping the basin covered during the attack by the acid so as to avoid loss by spurting. When the effervescence has ceased, evaporate the mixture to dryness.[2] Cool. Digest the residue with a little hot water and a few drops of hydrochloric acid. Heat the mixture to boiling and filter. Wash the residue on the filter-paper with hot water. Ignite and weigh as SiO_2.

2. *Alumina and Ferric Oxide.*—Precipitate the mixed ferric and aluminium hydroxides in the filtrate from the silica with ammonia and ammonium chloride in the usual way (page 164), and finally weigh as $Al_2O_3 + Fe_2O_3$.

3. *Calcium Carbonate.*—Acidify the filtrate from the ammonia precipitate with hydrochloric acid. Heat the solution to boiling, and, while still boiling, gradually add, crystal by crystal,[3] approximately 3 grms. of solid oxalic acid per gram of mixed calcium and magnesium oxides.[4] When all the oxalic acid has been added, add a slight excess of ammonia. Let the solution stand until the precipitate has settled—2 or 3 minutes.[5] According to Schoch,[6] a double precipitation is unnecessary; but if much magnesium be present, it is better to dissolve the washed calcium oxalate in hot hydrochloric acid and re-precipitate by the addition of ammonia and a little ammonium oxalate to the boiling solution. Filter the calcium oxalate and wash with cold water until

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hydrogen is supposed to be derived from the water. Note that hydrogen may come from the asbestos of the filter tube if the drying be imperfect, and also from the hydrated minerals. It is generally best to represent the result as "carbon derived from organic matter," without making any assumptions as to the composition of the organic matter. See page 644.

[1] K. J. Sundstrom, *Journ. Soc. Chem. Ind.*, **16**, 520, 1897; F. Hundeshagen, *Zeit. öffent. Chem.*, **15**, 85, 1909; N. Knight, *Chem. News*, **92**, 61, 108, 1905; **93**, 126, 1906; F. Clowes and J. B. Coleman, *ib.*, **92**, 259, 1905; W. H. Stanger and B. Blount, *Journ. Soc. Chem. Ind.*, **21**, 1216, 1902; Report, *ib.*, **21**, 12, 1223, 1902; G. Hentschel, *Chem. Ztg.*, **36**, 821, 1912.

[2] While the solution is evaporating, determine approximately the mixed calcium and magnesium carbonates as described below.

[3] Otherwise loss might occur from spurting. Stir all the time the acid is being added.

[4] The magnesium must all be converted to the oxalate to prevent the solution of calcium oxalate in the magnesium chloride (page 201). The approximate amount is determined from " 4," page 587.

[5] For more exact results, let stand overnight, or at least 3-4 hours.

[6] C. Schoch, *Die moderne Aufbereitung und Wertung der Mörtel-materialien*, Berlin, **36**, 1896; W. C. Blasdale, *Journ. Amer. Chem. Soc.*, **31**, 917, 1909; E. H. Schultze, *Chem. Ztg.*, **29**, 508, 1905; N. Busvold, *ib.*, **41**, 42, 1917; M. J. van Kruijs, *Chem. Weekblad*, **4**, 29, 1907; C. Liesse, *Ann. Chim. anal.*, **16**, 7, 1911; B. Enright, *Journ. Amer. Chem. Soc.*, **26**, 1003, 1904; C. Stolberg, *Zeit. angew. Chem.*, **17**, 741, 769, 1904; G. Lunge and M. Schochor-Tscherny, *ib.*, **7**, 481, 1894; *Tonind. Ztg.*, **18**, 661, 1894; R. F. Young and B. F. Baker, *Chem. News*, **86**, 148, 1902; R. Manzelius and A. Vesterberg, *Jahresber. Land. Inst. Ultuna*, **62**, 1894.

the washings are free from chlorides and oxalates.[1] Ignite the precipitate in a platinum crucible and finish the ignition with half an hour's blasting. Cool in a desiccator, and weigh as CaO.[2] Multiply the result by 1·7846 to get the corresponding amount of calcium carbonate.

4. *Mixed Calcium and Magnesium Carbonates.*—Weigh 1 grm. of the finely powdered sample into a small porcelain basin. Add 25 c.c. of N-HCl. Cover with a clock-glass and, when effervescence has ceased, heat the solution to boiling. When cold, titrate the free acid with N-NaOH and with a drop of methyl orange as indicator (page 58).

EXAMPLE.—After adding 25 c.c. of N-hydrochloric acid to 1 grm. of limestone, 5·15 c.c. of N-sodium hydroxide were needed to neutralise the excess of acid. Hence the mixed calcium and magnesium carbonates reacted with 19·85 c.c. of N-HCl. Again, 0·538 grm. of CaO was obtained. This corresponds with $1·7846 \times 0·538 = 0·9601$ grm. of CaCO$_3$. But 100·08 grms. of CaCO$_3$ react with 2000 c.c. N-HCl, thus 0·9601 grm. CaCO$_3$ will react with $0·9601 \times 2000/100·08 = 19·19$ c.c. N-HCl. Hence $19·85 - 19·19 = 0·66$ c.c. of N-HCl reacted with the magnesium carbonate. But 2000 c.c. N-HCl react with 84·32 grms. MgCO$_3$, thus 0·66 c.c. N-HCl reacts with $84·32 \times 0·66/2000 = 0·0278$ grm. MgCO$_3$. Hence the analysis reads (per cent.):

Calcium carbonate	96·01
Magnesium carbonate	2·78
Silica	1·06
Alumina and ferric oxide	0·00

The magnesium carbonate determined by this indirect process should not differ more than $\frac{1}{4}$ per cent. from that obtained by more elaborate methods.[3]

The Determination of Lime in the Presence of Aluminium, Iron and Phosphorus.—If the amount of lime only is needed, calcium oxalate can be precipitated in the presence of iron, aluminium, magnesium and phosphorus from a solution [4] the acidity of which has been adjusted to a p_H value of 4·0 to 4·5. Add to the hydrochloric acid solution 2 grms. of oxalic acid and about 5 grms. of ammonium chloride, followed by 10 drops of a 0·04 per cent. solution of bromocresol green. Dilute, if necessary, to about 200 c.c. Heat to boiling and add ammonia, drop by drop, until the colour changes to a pure green. Boil for a few minutes, stand on a water bath for 2 hours, filter, wash and ignite the calcium oxalate.[5]

[1] Magnesium can be determined in the combined filtrates, if desired, by the method of page 208. W. F. Koppeschaar, *Zeit. anal. Chem.*, 44, 184, 1905. The calcium oxalate can also be determined by the volumetric permanganate process (page 205). H. B. Kinnear, *Chem. Eng.*, 13, 247, 1911; H. Wdowiszewski, *Chem. Ztg.*, 38, 949, 1914; J. Mayrhofer, *Zeit. angew. Chem.*, 21, 592, 1908.

[2] The calcium oxide can be dissolved in 25 c.c. of N-HCl and titrated with N-NaOH in the usual manner (page 58), as a check on the weighings.

[3] A. S. Behrman, *Journ. Ind. Eng. Chem.*, 8, 42, 1916; N. Busvold, *Chem. Ztg.*, 41, 42, 1917.

[4] M. Passon, *Zeit. angew. Chem.*, 11, 776, 1898; 12, 1153, 1899; 14, 285, 1901; L. W. Winkler, *ib.*, 32, i, 24, 1919; J. F. Brezeale, *Journ. Assoc. Off. Agric. Chem.*, 4, 124, 1920; V. W. Meloche, L. E. Clifcorn and W. B. Griem, *ib.*, 16, 240, 1933; R. Nakaseko, *Mem. Coll. Sci. Kyoto*, 6, 157, 1923; W. F. Jakob, *Rocz. Chem.*, 3, 308, 1923; 5, 159, 1925; R. Mellet and E. Junker, *Schweiz. Apoth. Ztg.*, 62, 629, 645, 1924; E. Canals, *ib.*, 63, 29, 1925; J. Barlot, *Bull. Soc. chim.*, 25, 1026, 1924; F. L. Hahn and G. Weiler, *Zeit. anal. Chem.*, 70, 1, 1927; S. N. Rozanov and A. G. Filippova, *ib.*, 90, 340, 1932; W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, New York, 500, 1929; H. D. Chapman, *Soil Sci.*, 26, 479, 1928; R. Meurice, *Bull. Inst. agron. sta. Recherches Gembloux*, 1, 95, 1932; G. J. Cox and M. L. Dodds, *Ind. Eng. Chem. Anal. Ed.*, 4, 361, 1932; K. K. Jarvinen, *Zeit. anal. Chem.*, 43, 559, 1904; J. T. Dobbins and W. M. Mebane, *Journ. Amer. Chem. Soc.*, 52, 1469, 1930.

[5] R. K. Meade (*Chem. Eng.*, 1, 21, 1905; *Portland Cement*, Easton, Pa., 189, 1906) and K. Balthaser (*Chem. Ztg.*, 33, 646, 1909) describe volumetric processes for the determination of lime without the separation of silica, etc. For the volumetric determination of calcium in phosphates, see F. Kaminski, *Przemysl Chem.*, 13, 505, 1929.

Newberry's Process for the Simultaneous Determination of Magnesium and Calcium Carbonates.—Newberry [1] based a process for the volumetric determination of calcium and magnesium carbonates on the fact that magnesium hydroxide is sufficiently soluble in water to colour phenolphthalein, but when the solution is boiled with a dilute solution of sodium hydroxide, the magnesium is completely precipitated and separated from the calcium.

Transfer half a gram of limestone to an Erlenmeyer's flask, fitted with a long 'reflux condenser' (fig. 140, page 655). Add 60 c.c. of 0·2N-hydrochloric acid ("first acid"),[2] and boil the solution for 2 minutes with the condenser in position. Wash the interior of the condenser tube into the flask by means of a wash-bottle. Remove the tube and cool the solution thoroughly in a cooling-box (page 60). Add 5 drops of phenolphthalein solution and titrate with 0·2N-sodium hydroxide ("first alkali") until a faint pink colour appears in the solution. This may fade in a few seconds.[3]

Transfer the neutral solution to a large test tube (12 inches long and 1 inch internal diameter) provided with a mark [4] corresponding with 100 c.c. Heat the solution to boiling, add 0·2N-NaOH, 0·5 c.c. at a time, and boil after each addition. When a deep red colour is obtained which does not become paler on boiling, read the burette ("second alkali"). Dilute the solution to 100 c.c., boil for a moment and let the precipitate settle. When the precipitate has settled, pipette 50 c.c. of the clear solution into a flask and titrate with 0·2N-HCl until the pink colour has gone ("second acid").[5]

EXAMPLE OF CALCULATION.—Assume (1) that 11·6 c.c. of alkali ("first alkali") were needed for the first (cold) titration and (2) 3·55 c.c. of alkali ("second alkali") were used in the second (hot) titration. Assume further that 0·45 c.c. of acid were needed to neutralise the excess of alkali in 50 c.c. of the solution, after the second (hot) titration. Then $60·0 - 11·6 = 48·4$ c.c. of 0·2N-HCl were required to dissolve the mixed carbonates and $3·55 - (2 \times 0·45) = 2·65$ c.c. of 0·2N-NaOH were required to precipitate the magnesium as hydroxide. But since 1 c.c. of 0·2N-NaOH is equivalent to 1 c.c. of 0·2N-HCl, the volume of 0·2N-HCl used to dissolve respectively the calcium and magnesium carbonates in half a gram of the sample is (a) $48·4 - 2·65 = 45·75$ c.c., and (b) 2·65 c.c., *i.e.* 9·15 c.c. and 0·53 c.c. of 1·0N-HCl. Thus the percentage of calcium carbonate is $9·15 \times 200 \times 0·05 = 91·50$ and that of magnesium carbonate $0·53 \times 200 \times 0·042 = 4·45$.

If the results are to be expressed in terms of MgO and CaO, substitute 0·02 for 0·042 and 0·028 for 0·05, in the preceding formulæ.

The results for magnesium carbonate are usually a little high and for lime a little too low. This is probably due to the formation of calcium carbonate by the absorption of carbon dioxide from the air during the precipitation of magnesia and to the insolubility of the lime compounds in the sample. If much soluble alumina and iron be present, the end-point is obscured and the readings are more difficult. With the high-grade limestones the results are

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[1] S. B. Newberry, *Cement Eng. News*, **15**, 35, 1903; *Tonind. Ztg.*, **27**, 833, 1903; R. Willstätter and E. Waldschmidt-Leitz, *Ber.*, **56B**, 448, 1923; E. J. Pierce, *Journ. Ind. Eng. Chem.*, **7**, 163, 259, 1915; J. S. Pierce, W. C. Setzer and A. M. Peter, *ib.*, **20**, 436, 1928; J. S. Pierce and M. B. Geiger, *ib.*, *Anal. Ed.*, **2**, 193, 1930; A. C. Sheard and B. J. Heinrich, *ib.*, **2**, 388, 1930; A. C. Sheard and R. K. Valla, *ib.*, **4**, 246, 1932; G. A. Panchenko, *Ukrainskii Khem. Zhurnal*, **5**, (Sci. Pt.), 187, 1930; J. Moir, *Journ. Chem. Met. Min. Soc. S. Africa*, **17**, 129, 1917; *Journ. Soc. Chem. Ind.*, **36**, 571, 1917; S. S. Korol, *Journ. Applied Chem. (U.S.S.R.)*, **6**, 976, 1933.

[2] Standardised against Iceland spar.

[3] If the titration be carried until a permanent red coloration appears, the lime will be too low. If the limestone under investigation contains inappreciable amounts of magnesia, this completes the determination: (first acid ⁓ first alkali) $\times 40 \times 0·028 =$ the per cent. of CaO.

[4] A band of paper or etched ring.

[5] If more than 1 c.c. of acid be required, too much alkali was added and the magnesium hydroxide will have carried down some $Ca(OH)_2$.

suitable for technical work. With marble containing 54·62 per cent. CaO and 0·84 per cent. MgO by the gravimetric process, 54·99 and 0·88 respectively were obtained by Newberry's process. With a magnesian marl containing 5·43 per cent. of alumina and ferric oxide, 52·08 per cent. of silica, 19·52 per cent. of CaO and 2·24 per cent. of magnesia, Newberry's process gave:—

| CaO | . | . | 17·02 | 16·83 | 17·36 per cent. |
| MgO | . | . | 2·08 | 2·30 | 2·00 per cent. |

For a sample of dolomitic marl with 26·50 per cent. CaO and 18·76 MgO—

| CaO | . | . | 26·38 | 25·42 | 25·53 per cent. |
| MgO | . | . | 17·80 | 18·40 | 18·96 per cent. |

were obtained. Experiments with artificial mixtures of Iceland spar and magnesium carbonate gave excellent results. The results with the less pure limestones and calcareous marls are not so good.

Magnesite. – In the case of magnesites,[1] the joint magnesia and lime [2] may be determined by boiling 0·5 grm. of the magnesite with a known excess of standard sulphuric acid and titrating back the excess with standard sodium hydroxide. The lime can be precipitated from the solution by adding an excess of 90 per cent. alcohol—250 c.c. of alcohol per 100 c.c. of the solution. Let the mixture stand in a covered vessel overnight. Filter and wash with 50 per cent. alcohol, and proceed as indicated in footnote 1, page 202. After subtracting the calcium oxide from the joint magnesium and calcium oxides obtained by the titration, the amount of magnesia follows at once. The magnesia may exist in the form of oxide, hydroxide or carbonate.[3] The hydroxide can be determined from the loss in weight which occurs when the sample is baked to a constant weight at 300°–350° and the carbonate from the loss in weight which occurs when the same sample is calcined to constant weight at a red heat. The difference between the amounts so determined and the total magnesia represents the magnesium oxide. The water and carbon dioxide can be determined by the more laborious processes, pages 631

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[1] For a volumetric process, see *Chem. Ztg.*, **33**, 545, 1909. V. Macri (*Boll. Chim. Farm.*, **57**, 301, 1918) condemns this method.

[2] If the amount of calcium relative to the magnesium is very small, O. Kallauner and I. Preller (*Chem. Ztg.*, **36**, 449, 462, 1912) show that the oxalate process (pages 202–3) is trustworthy only if (1) dilute solutions are used, (2) a large excess of ammonium salts and ammonium oxalate are present, (3) the solution is filtered immediately after precipitation, or (4) if the precipitation is repeated: otherwise the lime is always 0·15 to 0·2 per cent. low, owing to re-solution during washing. Most methods involving the precipitation of calcium sulphate in alcoholic solutions are unreliable if much magnesia is present. Good results are obtained as follows: (1) Precipitate the lime as oxalate, filter and wash, convert the oxalate into sulphate, dissolve the sulphate in hydrochloric acid, reprecipitate as oxalate and weigh as CaO. Or (2), evaporate a solution of the mixed chlorides to dryness with lithium sulphate, treat the residue with a mixture of 10 volumes of ethyl alcohol and 90 volumes of methyl alcohol saturated with lithium sulphate. The precipitated calcium sulphate is dissolved in hydrochloric acid and reprecipitated by the oxalate process—E. C. Carron, *Ann. Chim. anal.*, **17**, 127, 1912; R. Hefelmann, *Zeit. öffentl. Chem.*, **3**, 193, 1897; K. J. Sundstrom, *Journ. Soc. Chem. Ind.*, **16**, 560, 1897.

[3] For the total magnesia in magnesites, J. Mayrhofer (*Zeit. angew. Chem.*, **21**, 592, 1908) decomposes 5 grms. of the finely powdered mineral with aqua regia on a water bath. Evaporate the solution to dryness to render the silica insoluble. Digest with acidulated water, filter and make the solution up to a litre; mix 40 c.c. (20 c.c. if burnt magnesite is in question) with 5 c.c. dil. sulphuric acid and 100 c.c. citrate-solution (100 grms. citric acid, 333 c.c. of ammonia—sp. gr. 0·91—made up to a litre with water), 20 c.c. of a 10 per cent. solution of disodium hydrogen phosphate and 15 c.c. of ammonia. Stir the mixture 5 minutes without touching the walls of the beaker. Filter, etc., after standing 5 minutes. The calcium is not precipitated in presence of the ammonium citrate. Compare N. A. Tananaev and V. M. Tarayan, *Zavodskaya Lab.*, **3**, 112, 1934.

et seq.[1] The value of burnt magnesia depends upon the proportion of "active magnesia." The "active magnesia" is the difference between the total magnesia, MgO, and that combined with carbon dioxide and water.[2]

§ 289. The Mineralogical Analysis of Limestones and Marls.

Calcium carbonate is undoubtedly the prevailing constituent of limestone rocks, and magnesium carbonate is probably next in importance. With increasing proportions of the latter, the carbonate rock passes into dolomite, magnesian limestone and finally magnesite. Ferrous and manganese carbonates are usually present in small quantities and when these compounds predominate, siderite and other ores of iron and manganese result. It is usual, in technical analysis, to report the lime and magnesia as carbonates and the iron and manganese as oxides. In all probability, the two latter more generally exist as carbonates. A determination of the carbon dioxide will sometimes show that more carbon dioxide is present than is required for the lime and magnesia. Some of the lime and magnesia may also be combined with the silica and alumina and, in consequence, even if the amount of carbon dioxide does satisfy the lime and magnesia, some may be combined with the iron and manganese. Phosphorus may be combined with the iron and aluminium or be present as apatite. The silicate minerals associated with the calcareous clays and limestones are probably as varied as the silicate minerals found in clays (*q.v.*).[3]

Many attempts have been made to isolate the different minerals in limestones and marls by treatment with different solvents. Struckmann[4] analysed various marls by digesting the samples first with water, then with acetic acid and finally with hydrochloric acid. Each solution and the residue was examined separately. Bolton[5] studied the action of citric and tartaric acids, and Jannettaz[6] the action of potassium bisulphate. Deville[7] tried to dissolve calcium carbonate from mortars by boiling the mixture with a solution of ammonium nitrate, which he supposed did not attack the silicates, but Gunning showed that Deville's assumption is faulty. Browne and Harrison's[8] method of dealing with the problem is as follows:—

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[1] For the determination of magnesia in the presence of magnesium carbonate from the heat of the reaction with hydrochloric acid, see V. Fortini, *Chem. Ztg.*, **36**, 270, 1912.

[2] O. Kallauner, *Chem. Listy*, **20**, 549, 1926; *Chem. Ztg.*, **36**, 711, 1912; L. Dede, *ib.*, **36**, 414, 1912.

[3] W. F. Hume, *Chemical and Mineralogical Researches on the Upper Cretaceous Zones of the South of England*, London, 1893; S. Pfaff, *Zeit. Gesammt. Naturwiss.*, (3), **3**, 273, 1878; L. Cayeux, *Ann. Soc. Géol. du Nord*, **16**, 342, 1890; A. Vesterberg, *Bull. Geol. Inst. Upsala*, **5**, 97, 1900; **6**, 254, 1904; K. Haushofer, *Sitzber. K.K. Akad. Wiss. München*, **11**, 220, 1881.

[4] C. Struckmann, *Liebig's Ann.*, **74**, 170, 1858; C. J. B. Karsten, *Archiv Min.*, **22**, 592, 607, 613, 1848; E. Damour, *Bull. Soc. Geol.*, (2), **6**, 313, 1849; G. Forchhammer, *Journ. prakt. Chem.*, (1), **49**, 55, 1850; J. Roth, *Zeit. deut. geol. Ges.*, **4**, 565, 1852; T. Liebe, *ib.*, **7**, 406, 1855; F. Hoppe-Seyler, *ib.*, **27**, 499, 1875; F. Pfaff, *Pogg. Ann.*, **82**, 488, 1851; T. S. Hunt, *Amer. J. Science*, (2), **28**, 181, 371, 1859; M. Schafhäutl, *Neues Jahrb. Min.*, 812, 1864; C. Knausz, *Chem. Centr.*, (1), **26**, 244, 1855; C. Doelter and R. Hörnes, *Jahrb. geol. Reichsanst.*, **69**, 1875; C. Schmidt, *N. Petersb. Acad. Bull.*, **16**, 205, 1871.

[5] H. C. Bolton, *Ann. N.Y. Acad. Science*, **1**, 1, 153, 1877–80; *Proc. Amer. Assoc. Adv. Science*, **31**, 271, 1883; *Chem. News*, **36**, 249, 1877; **37**, 14, 24, 65, 86, 98, 1878; **38**, 168, 1878; **43**, 31, 39, 1881; **47**, 251, 1883; J. W. Richards and N. S. Powell, *Journ. Amer. Chem. Soc.*, **22**, 117, 1900.

[6] E. Jannettaz, *Compt. rend.*, **77**, 838, 1873; **78**, 852, 1874.

[7] H. St C. Deville, *Compt. rend.*, **37**, 1001, 1853; J. W. Gunning, *Journ. prakt. Chem.*, (1), **62**, 318, 1854.

[8] A. J. J. Browne and J. B. Harrison, "On the Geology of Barbados," *Quart. Journ. Geol. Soc.*, **48**, 170, 1892.

Clay and Quartz.—Digest 5 grms. of the air-dried and powdered sample in dilute hydrochloric acid (2·5 per cent.) [1] in the cold (30°). When effervescence has ceased, decant the solution through a filter-paper. Heat the residue on a water bath several hours with a concentrated solution of sodium carbonate containing some sodium hydroxide [2] and wash the residue at the filter pump (1) with the same solution; (2) with water; and (3) with dilute hydrochloric acid. Ignite and weigh the residue as "clay and siliceous minerals."

Reduce the residue to an impalpable powder in an agate mortar and boil a weighed portion repeatedly with concentrated sulphuric acid until the clay is quite decomposed. Drive off the excess of acid and heat the residue with dilute hydrochloric acid to dissolve basic aluminium and ferric sulphates. Filter and wash. Heat the residue with the sodium carbonate solution to dissolve the colloidal silica set free during the decomposition of the clay. Again filter, wash and ignite the residue. The final residue represents the crystalline siliceous minerals, mostly quartz. The difference between the weight of "clay and siliceous minerals" and the weight of the quartz residue obtained therefrom, multiplied by 1·1623, represents the amount of clay, provided it be assumed that the clay can be represented by $Al_2O_3 . 2SiO_2 . 2H_2O$, and that ignited clay is all dissolved by the treatment in question. For the limitations involved in this assumption see pages 758 *et seq.*

Colloidal Silica.—Treat 5 grms. of the air-dried and powdered sample with dilute hydrochloric acid (2·5 per cent.) in the cold (30°). Evaporate the solution to dryness in a porcelain basin, with the usual precautions against loss by spurting (page 147), in order to render the silica insoluble. Digest the residue in warm hydrochloric acid, add water, filter and wash. Ignite the residue and weigh. The insoluble matter consists of the residue insoluble in dilute hydrochloric acid, together with the colloidal silica originally present in the sample and that formed by the decomposition of certain hydrated silicates and aluminium silicate, which may be present in small quantities. The difference between the weight of this mixture and the "clay and quartz" resulting from the preceding operation represents the colloidal silica.[3]

EXAMPLE.—Suppose that 5 grms. of gault clay furnished:

Clay and quartz residue	0·2514 grm.
Quartz residue	0·1255 grm.
Calcined clay	0·1259 grm.
Siliceous residue	0·3819 grm.
Clay and quartz residue	0·2514 grm.
Colloidal silica	0·1305 grm.

The calcined clay corresponds with $0·1259 \times 1·1623 = 0·1463$ grm. of clay. Hence the sample would be reported to contain:

Quartz residue	2·51 per cent.
Clay residue	2·93 per cent.
Colloidal silica	2·61 per cent.

[1] Dilute acetic acid was tried, but it only partially attacked the zeolites and the silica set free from these minerals was estimated as colloidal silica.

[2] LUNGE'S SOLUTION.—Dissolve 100 grms. of crystalline sodium carbonate and 10 grms. of sodium hydroxide in water and make the solution up to a litre with water. Remember that the solution will dissolve silica from the glass of any bottle in which it may be stored.

[3] The term "colloidal silica" is here synonymous with "silica soluble in dilute hydrochloric acid." Note that burnt limestones and burnt magnesites may contain more "soluble silica" than the raw material, owing to the formation, during calcination, of silicates, which can be decomposed by treatment with acids.

Alumina, ferric oxide, etc., can be determined in the filtrate from the silica in the usual way.[1]

Clay in Limestones.—A number is obtained by the following process which is generally supposed to represent the amount of "clay" in the given limestone:—Digest 2 grms. of the powdered sample with 40 c.c. of water and 4 c.c. of concentrated hydrochloric acid as indicated on page 591. When effervescence has ceased, boil the solution for about 10 minutes to drive off the carbon dioxide. Precipitate any iron and aluminium which may have gone into solution by the addition of ammonia. Filter through a Gooch crucible, wash, ignite at a low red heat and weigh. Between one and two hours are required for the determination. Archetti[2] considers that, if much magnesia be present, the results will be high, because some magnesium hydroxide will be precipitated by the ammonia. In such cases, Archetti treats 2 grms. of the sample with 10 per cent. hydrochloric acid mixed with one-tenth its volume of 10 per cent. nitric acid. When solution is complete, add an excess of ammonium chloride and a slight excess of ammonia. Wash the precipitate, etc., as before.[3]

§ 290. The Determination of Free Lime in Quicklime and Mortars.

Free lime may be detected in whiting by boiling a couple of grams for about 5 minutes with 100 c.c. of water. An alkaline reaction—development of a red colour with phenolphthalein - is generally taken to represent free lime, although the coloration may possibly be due to the partial hydrolysis of the carbonate and to the presence of alkali hydroxides or carbonates in the original sample.

Winkler's Process.—To determine the free lime in quicklime,[4] carefully slake 10 grms. of the sample with water, transfer the resulting cream to a 250 c.c. flask and make the contents up to the mark with distilled water. Pipette 25 c.c. (=1 grm. of the sample) of the thoroughly mixed contents into an Erlenmeyer's flask, add a few drops of phenolphthalein[5] as indicator and titrate slowly with N-hydrochloric acid until the red colour disappears. The colour change takes place before the calcium carbonate is attacked by the acid and it is possible to strike the point where all the calcium hydroxide is just neutralised. The small amount of carbon dioxide liberated by the next drop or two of the standard acid decolorises the phenolphthalein and indicates the end of the titration. The acid must be added very slowly with constant stirring to get reliable results.

Stone and Schenck's Process.[6]—This is based on the fact that calcium oxide

[1] For phosphoric acid in limestones, see F. Hinden, *Zeit. anal. Chem.*, **54**, 214, 1915.

[2] A. Archetti, *Boll. Chim. Farm.*, **48**, 409, 1909.

[3] For the analysis of mortars, see W. J. Dibdin and R. Grimwood, *Analyst*, **21**, 197, 1896; for peat soils, R. A. Gortner, *Soil Sci.*, **1**, 505, 1916; J. L. Heitzman, *Eng. News Record*, **97**, 271, 1926; D. Florentin, *Compt. rend.*, **183**, 53, 1926.

[4] Also in slaked lime. A. Winkler, *Journ. prakt. Chem.*, (1), **67**, 444, 1856; W. Richter, *Tonind. Ztg.*, **27**, 1862, 1943, 1903.

[5] A. Gawalovski, *Zeit. anal. Chem.*, **22**, 397, 1883; F. W. Küster, *Zeit. anorg. Chem.*, **13**, 141, 1897; G. Lunge, *Zeit. angew. Chem.*, **10**, 41, 1897; C. Winkler, *Praktische Uebungen in der Maassanalyse*, Leipzig, 1888. For phenacetolin as indicator, see G. Lunge, *Chem. Ind.*, **4**, 349, 1881; *Journ. Soc. Chem. Ind.*, **1**, 56, 1882. A 0·2 per cent. aqueous solution is used. The solution is pale yellow in the presence of caustic alkalies and brick red with alkali carbonates and magnesia—P. Degener, *Zeit. Ver. Rübenzucker Ind.*, **31**, 357, 1881; *Chem. Ztg.* **5**, 400, 1881.

[6] W. E. Stone and F. C. Schenck, *Journ. Amer. Chem. Soc.*, **16**, 721, 1894; *Chem. News*, **70**, 278, 1894; J. Hendrick, *Analyst*, **32**, 320, 1907. For the solubility of lime in saccharine solutions, see J. Weisberg, *Bull. Soc. chim.*, (3), **21**, 773, 1899; **23**, 740, 1900; *Chem. News*,

forms soluble compounds with a solution of cane sugar under conditions where calcium carbonate, alumina and ferric oxide remain unaffected. Hence shake, say, 1 grm. of the powdered sample with 500 c.c. of a 10 per cent. solution of cane sugar for 20 minutes. Filter and wash with the solution of sugar. The lime in the filtrate can be determined either by precipitation as calcium oxalate, or volumetrically by titration with standard hydrochloric acid. The authors say that "magnesia is not soluble to any appreciable extent in the solution of cane sugar containing lime, under the stated conditions."

Frühling's Method.[1]— 5 grms. of the powdered sample are introduced into a stoppered Erlenmeyer's flask. Add 100-150 c.c. of water and 30 drops of phenolphthalein solution. Shake the contents thoroughly. Wash the sides of the flask and the stopper. Add, say, 30 c.c. of standard hydrochloric acid [2] from a burette. The red colour of the solution may disappear, but it will reappear if the flask be agitated, because "quicklime" generally contains more than 60 per cent. of CaO. Add a gram of ammonium chloride. The remaining calcium hydroxide decomposes the ammonium salt, liberating an equivalent amount of ammonia. This facilitates subsequent titration. Add the hydrochloric acid 1 c.c. at a time until the red colour takes an appreciable time to return when the flask is agitated. The acid is now added 0·1 c.c. at a time. If the red colour does not appear after the agitated solution has stood 5 minutes, read the volume of acid used and multiply the result by 2 to get the corresponding amount of CaO in the given sample. For instance, if 38 c.c. of hydrochloric acid had been used, the sample contained 76 per cent. of CaO. Frühling's process is also applied to the determination of lime in mortar.[3] The mortar is well mixed by passing it through a sieve with a stiff brush. Weigh 100 grms.[4] into a stoppered flask. Add 25 grms. of ammonium chloride, 100 c.c. of water and 20 drops of phenolphthalein. Add 50 c.c. of the standard hydrochloric acid. The red colour disappears temporarily but reappears on shaking. This shows that free lime is still present. Continue adding acid 1 c.c. at a time until the red colour reappears but slowly. Then add the acid in smaller portions at a time, say 0·5 c.c. Finally, when the red colour does not appear until the solution has stood for 5 minutes, the titration is complete and the calculation is made as before.[5]

Estimates of the free lime in cements are apt to be misleading, because no method is yet known which is universally applicable. Some of the

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82, 284, 1900. See also W. Heldt, *Journ. prakt. Chem.*, (1), **94**, 129, 1865; L. C. Levoir, *Rec. Trav. chim.*, **5**, 59, 1886; C. Parsons, *Deut. Töp. Zeig. Ztg.*, **2**, 585, 1888; W. P. Mason, *Journ. Amer. Chem. Soc.*, **16**, 733, 1894; O. Rebbufat, *Tonind. Ztg.*, **23**, 782, 823, 883, 900, 1899; *Gazz. Chim. Ital.*, **28**, ii, 209, 1899; W. H. Low, *Chem. Engineer*, **4**, 13, 1906.

[1] R. Frühling, *Tonind. Ztg.*, **8**, 393, 1884; H. Seger and E. Cramer, *ib.*, **31**, 619, 1907; W. E. Emley, *Journ. Amer. Cer. Soc.*, **17**, 720, 1915.

[2] 1000 c.c. of the hydrochloric acid have 130·0 grms. of HCl, and this is equivalent to 100 grms. of CaO. Hence 1 c.c. of the standard solution corresponds with 0·1 grm. of CaO.

[3] M. Holmblad, *Tonind. Ztg.*, **13**, 143, 1889; H. Seger and E. Cramer, *ib.*, **26**, 1719, 1902.

[4] A small brass cylinder, closed at one end, and fitted with a movable piston, is sometimes used when the mortar is evaluated by volume, not by weight. The cylinder holds 50 c.c. of mortar and it is filled by placing the mouth of the cylinder with the piston depressed into the mass of mortar. By elevating the piston and pressing the cylinder into the mortar, the cylinder is easily filled. By depressing the piston, 50 c.c. of mortar can be delivered into a glass cylinder for analysis. The final result is then represented as kilograms (or lbs.) per cubic metre (or cubic foot).

[5] If the sand mixed with the lime contains calcium carbonate, the lime content of the mortar may come out too high, because some of the acid may have attacked the carbonate. The calcium hydroxide is, however, attacked before the carbonate, as indicated under "Winkler's process," above. See H. E. Kiefer, *Journ. Ind. Eng. Chem.*, **4**, 358, 1912; A. H. White, *ib.*, **1**, 6, 1909.

calcium silicates and aluminates are decomposed, by hydrolysis, at the same time as the "free lime" is dissolved. Solutions of glycerol[1] in water, iodine solutions,[2] dilute hydrochloric acid,[3] ammonium salts[4] (page 590) and other reagents[5] have been proposed and found unsatisfactory. The same might be stated concerning the attempt to determine this constant from the amount of "heat" developed during hydration.[6]

For determining the lime in slaked lime, containing the oxide, hydroxide and carbonate, Weissenberger[7] recommends first drying the material for 30 minutes at 120° in an atmosphere free from carbon dioxide. The lime is then slaked and similarly dried. The weight of the substance before and after

[1] F. Hart, *Tonind. Ztg.*, **24**, 1674, 1900; M. Mayard, *Bull. Soc. chim.*, (3), **27**, 851, 1902; *Chem. News*, **87**, 109, 1903. A mixture of glycerol and alcohol is now commonly used—G. E. Bessey, *Cement*, **9**, 163, 1936; L. T. Work and F. P. Lasseter, *Concrete (Cement Mill. Ed.)*, **38**, No. 3, 81; No. 4, 89; No. 5, 79, 1931.

[2] F. Hart, *Dingler's Journ.*, **175**, 208, 1865.

[3] C. Zulkowsky, *Tonind. Ztg.*, **22**, 285, 1898; H. Hauenschild, *ib.*, **19**, 239, 1895; E. Fremy, *Compt. rend.*, **67**, 1205, 1868; E. Laudrin, *ib.*, **96**, 156, 379, 841, 1229, 1883; F. Schott, *Dingler's Journ.*, **202**, 434, 1871; G. Feichtinger, *ib.*, **174**, 437, 1864; A. Schulatschenko, *ib.*, **194**, 355, 1869.

[4] G. Berju and W. Kosinenko (*Landw. Ver. Stat.*, **60**, 419, 1904; A. Bodenbender and E. Ihlee, *Zeit. Ver. Rübenzuckerind.*, **29**, 714, 1907) use ammonium nitrite; M. Heyer (*Chem. Ztg.*, **33**, 102, 1157, 1909; P. Philossophoff, *ib.*, **33**, 67, 1909; M. Popel, *Zeit. angew. Chem.*, **21**, 2080, 1908; F. Knapp, *Dingler's Journ.*, **265**, 184, 1887; M. Toméi, *Tonind. Ztg.*, **19**, 177, 1895; H. Hauenschild, *ib.*, **19**, 239, 1895; S. Wormser, *ib.*, **24**, 1636, 2072, 1900; E. Michel, *Journ. prakt. Chem.*, (1), **33**, 548, 1844; R. S. Beall, *Chem. Engineer*, **3**, 315, 1906; W. H. Low, *ib.*, **4**, 13, 1906; H. Cantoni and G. Gorguélia, *Chem. News*, **90**, 4, 1904; A. Cavazzi, *Ann. Chim. appl.*, **4**, 137, 1915; H. Schreib, *Zeit. angew. Chem.*, **2**, 211, 1889) uses ammonium chloride; R. Brandenberg (*Chem. Ztg.*, **33**, 880, 1909) distils with an alcoholic solution of ammonium bromide. The ammonia in the distillate corresponds with the calcium oxide. J. Hendrich (*Journ. Soc. Chem. Ind.*, **28**, 775, 1909; **30**, 520, 1911) determined the free lime in basic slags by distilling them with solutions of ammonium sulphate and chloride, and estimated the basicity of the slag from the amount of ammonia given off: $(NH_4)_2SO_4 + CaO = CaSO_4 + H_2O + 2NH_3$. The ammonia evolved owing to the hydrolysis of the ammonium salts (W. Smith, *Journ. Soc. Chem. Ind.*, **15**, 3, 1896; **30**, 253, 1911; V. H. Veley, *Journ. Chem. Soc.*, **87**, 26, 1905; A. Vürtheim and G. H. Jongen, *Chem. Weekb.*, **28**, 206, 1931) is negligibly small, and he claims the results are satisfactory. G. Feichtinger (*Bayer. Kunst. Gewerb.*, 69, 1858) used ammonium carbonate; M. Tomei (*Tonind. Ztg.*, **19**, 177, 1895) used ammonium hydroxide, and also ammonium acetate; S. Wormser (*Tonind. Ztg.*, **24**, 28, 1900), ammonium oxalate. See also A. Winkler, *Dingler's Journ.*, **175**, 208, 1865.

[5] M. Bischoff (*Chem. Ztg.*, **27**, 33, 1903) recommends water for extracting lime from slags, since he thinks sugar solutions dissolve calcium hydrogen carbonate. E. H. Keiser and S. W. Forder (*Amer. Chem. Journ.*, **31**, 153, 1904; A. S. Cushman, *ib.*, **31**, 445, 1904) propose to determine lime in commercial quicklime, slags and cements by digesting with water—free lime is attacked at once, calcium silicates but slowly (A. Winkler, *Chem. Centr.*, (2), 481, 1858; H. le Chatelier, *Bull. Soc. chim.*, (2), **41**, 377, 1884; L. C. Levoir, *Rec. Trav. chim.*, **5**, 59, 1886; C. Zulkowsky, *Chem. Ind.*, **24**, 290, 1901); water and carbon dioxide (G. Feichtinger, *Dingler's Journ.*, **174**, 437, 1864; A. Winkler, *l.c.*; L. C. Levoir, *l.c.*); lime-water (E. Laudrin, *l.c.*; H. le Chatelier, *l.c.*); sodium carbonate (G. Feichtinger, *Bayer. Kunst. Gewerb.*, 69, 1858; F. Schott, *Dingler's Journ.*, **202**, 434, 1871); potassium carbonate (G. Oddo and E. Manselle, *Gazz. Chim. Ital.*, **25**, ii, 101, 1895; G. Feichtinger, *l.c.*); sodium hydroxide (F. Hart, *Tonind. Ztg.*, **24**, 1674, 1900); magnesium chloride (F. Knapp, *Dingler's Journ.*, **265**, 184, 1887); magnesium nitrate (C. Zulkowsky, *Zeit. Niederösterreich Ing. Ver.*, 1863); calcium chloride (L. C. Levoir, *Rec. Trav. chim.*, **4**, 55, 1885); aluminium chloride (S. Wormser and O. Spanjer, *Tonind. Ztg.*, **23**, 1785, 1899); water glass (W. Heldt, *Journ. prakt. Chem.*, (1), **94**, 129, 1865); hydrogen sulphide (B. Steuer, *Tonind. Ztg.*, **23**, 1604, 1899); ethylene glycol (P. Schläpfer and R. Bukowskii, *Eidgenoss Materialprüfungsanstalt E.T.H. Zürich*, Report No. 63, 1933; D. R. MacPherson and L. R. Forbrich, *Ind. Eng. Chem. Anal. Ed.*, **9**, 451, 1937).

[6] W. Ostwald and R. Blank, *Riga Ind. Ztg.*, **9**, 208, 1883; V. Fortini, *Ann. Lab. Chim. Centr. Gabelle*, **6**, 509, 1912.

[7] G. Weissenberger, *Oester. Chem. Ztg.*, **16**, 192, 1913. For the determination of free magnesia in cements, see B. Grünwald, *Chem. Ztg.*, **37**, 885, 1913.

slaking gives the necessary data for calculating the amount of calcium oxide. Estimation of the hydroxide from the loss of water on ignition gives high results because the dried hydroxide always contains a little more water than corresponds to $Ca(OH)_2$. If the amount of hydroxide is small this does not matter. Calcium hydroxide also has an appreciable vapour pressure at 120°.

§ 291. The Analysis of Calcium Sulphate, Plaster of Paris and Gypsum.

Gypsum, terra alba and plaster of Paris are more or less pure varieties of calcium sulphate. The analysis of calcium sulphate generally involves the determination of lime (CaO), sulphur trioxide (SO_3), water, silica, iron and aluminium oxides, magnesia and carbon dioxide.[1] Calcining and physical tests show the value of gypsum and plaster of Paris better than chemical analysis. For the loss of moisture when grinding the sample, see page 107.

Moisture. — Heat about a gram of the sample one hour at 105° and note the loss in weight.[2] Heat a weighed amount of the sample (say, 1 grm.) in a crucible, first on a hot plate, then at a dull red heat over a Bunsen burner for about 10 minutes, and at a rather lower temperature for about 40 minutes. Cool and weigh. Repeat the ignition until a constant weight is obtained. This gives the total water.

EXAMPLE.—Suppose that:

Crucible and 1 grm. of raw gypsum	20·2682 grms.
Crucible and gypsum after 105° (1 hr.) . . .	20·1114 ,,
Crucible and gypsum after 105° ($\frac{1}{2}$ hr. more) . .	20·1113 ,,
Water lost at 105°	0·1569 grm.
Crucible and raw gypsum	20·2682 grms.
Crucible and gypsum after dull redness . . .	20·0592 ,,
Total water	0·2090 ,,
Water lost at 105°	15·69 per cent.
Total water.	20·90 ,,

Frey's Process for the Different Forms of Plaster.—In view of the different forms of plaster on the market, it is necessary to determine the different modifications[3] of plaster in a given sample. The problem, at present, has not been solved completely, but Frey[4] has made the best attempt. The hemihydrate— $CaSO_4.\frac{1}{2}H_2O$—is estimated by finding the amount of water taken up at ordinary temperatures and retained at 60°. 5 grms. of the sample are spread in a thin layer over the bottom of a porcelain basin and just covered with water from a wash-bottle. In 30 minutes, the basin is placed in a drying oven at 60° and kept at that temperature until the weight is constant. If a grms. of water are taken up, the weight y of hemihydrate in the sample is

$$y = 5·371a \quad . \quad . \quad . \quad . \quad . \quad (1)$$

[1] E. H. S. Bailey, *Univ. Geol. Sur. Kansas*, 5, 166, 1899; A. Cavazzi, *Gazz. Chim. Ital.*, 43, ii., 71, 1913; *Ann. Chim. appl.*, 6, 18, 1916; G. Gallo, *Gazz. Chim. Ital.*, 44, i., 497, 1914; P. P. Budnikov, *Journ. Amer. Cer. Soc.*, 7, 817, 1924.

[2] Gypsum—$CaSO_4.2H_2O$—begins to lose water at 40°; three-fourths of its water is driven off at 155° and at 194° the anhydrous sulphate is formed. Gypsum heated to about 400° forms "dead burnt" and flooring plaster. V. Zunino, *Gazz. Chim. Ital.*, 30, i., 333, 1900. G. Surr (*Min. Eng. World*, 36, 467, 1912) recommends reporting as "moisture" the loss of weight gypsum suffers on heating to 80°, and "combined water" at 200°.

[3] For the five different modifications, see J. H. van't Hoff, *Zeit. phys. Chem.*, 45, 257, 1903; P. Rohland, *Zeit. anorg. Chem.*, 35, 201, 1903; 36, 332, 1903.

[4] O. Frey, *Tonind. Ztg.*, 33, 1229, 1909.

unless soluble anhydrite be also present. In that case, the weight of the anhydrite z must be taken into account from (3) below:

$$y = 5 \cdot 371(a - 0 \cdot 265z) \quad . \quad . \quad . \quad . \quad (2)$$

The soluble anhydrite is estimated by exposing 5 grms. of the sample in a thin layer as before to water vapour at the ordinary temperature for a period of 7 days under a bell-jar. The whole of the soluble anhydrite is thus converted into hemihydrate, and if b represents the increase in weight after drying at 60°- 70°,

$$z = 15 \cdot 113b \quad . \quad . \quad . \quad . \quad . \quad (3)$$

To detect soluble anhydrite, a portion of the plaster is lawned into a small cylinder containing 200 c.c. of water in which a sensitive thermometer is immersed. If soluble anhydrite be present, the temperature rises almost at once and continues to rise for about 2 minutes. The rise of temperature which occurs when the hemihydrate is alone present begins some 5 minutes after the mixing and continues for about 20 minutes.

The proportion of flooring plaster [1] found in plaster of Paris which has been burnt at too high a temperature is estimated by wetting 5 grms., as in the estimation of the hemihydrate, allowing it to remain 7 days in a moist atmosphere, and finally drying at 60°. If c denotes the increase in weight, the amount e of the flooring plaster is

$$e = 3 \cdot 778(c - a) \quad . \quad . \quad . \quad . \quad (4)$$

The constituents indicated above are all capable of hydration but, in addition to these active components, the sample may contain unburnt gypsum, dead-burnt plaster, natural anhydrite and impurities—clay and sand. The unburnt plaster is estimated by finding the loss in weight on ignition. If the loss in weight be w, the weight of unburnt gypsum r is

$$r = 4 \cdot 778(w - 0 \cdot 062y) \quad . \quad . \quad . \quad . \quad (5)$$

If the total calcium sulphate as determined from the weight of the sulphate present is S, the weight t of natural anhydrite and of dead-burnt plaster is then

$$t = S - (0 \cdot 938y + z + e + 0 \cdot 791r) \quad . \quad . \quad . \quad (6)$$

The sand and clay are determined by difference.

Silica. —Digest 1 grm. of the powdered sample in an evaporating basin with 20 c.c. of concentrated hydrochloric acid and 20 c.c. of water. Evaporate the solution to dryness. Boil the mass several times [2] with 100 c.c. of dilute hydrochloric acid (1 : 3). Filter and collect the insoluble matter on a filter-paper, wash with hot water, ignite, weigh and report as insoluble siliceous minerals, or treat the residue as in a clay analysis with hydrofluoric acid.[3]

Alumina and Ferric Oxide.—Make the filtrate up to 500 c.c. in a measuring flask. Transfer 300 c.c. to a 600 c.c. Erlenmeyer's flask. Precipitate the

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[1] Flooring or hydraulic plaster—*Estrichgips*—is gypsum which has been calcined at about 400° and which has accordingly lost all its water but, unlike "dead-burnt plaster," is able to combine with water to form a cement. Flooring plaster and dead-burnt plaster are both dehydrated, but the former is active and admits of rehydration, the latter is inactive. J. H. van't Hoff and J. Just, *Sitzber. K. Preuss. Akad. Wiss.*, I, 249, 1903.

[2] A single boiling may not suffice to dissolve all the calcium sulphate. There is here a danger of error owing to some calcium sulphate escaping solution.

[3] Or fuse the residue with sodium carbonate; digest with hydrochloric acid; evaporate to dryness for silica; digest the dry mass with dilute hydrochloric acid; filter, wash and add the filtrate to the main solution.

ferric and aluminium hydroxides with ammonia, ignite the washed precipitate with the residue left after treating the siliceous residue with hydrofluoric acid.

Lime and Magnesia.—The filtrate from the ammonia precipitate is concentrated by evaporation and the lime and magnesia determined in the usual way (pages 202 and 208).

Sulphuric Acid.—The 200 c.c. remaining in the measuring flask are treated with barium chloride as described on page 703. The amount of barium sulphate, multiplied by 0·5832, represents the corresponding amount of calcium sulphate; and by 0·2403 gives the corresponding amount of CaO. If the amount of CaO so determined is less than the amount obtained by the oxalate process, the remaining CaO will probably have been combined with carbon dioxide; and the amount of calcium carbonate is determined by multiplying the difference between the two results by 1·7847. Carbon dioxide is not usually present. If it is, the amount can be determined by the process described on page 624.

EXAMPLE.—Suppose that the analysis of a sample of gypsum gave.

Barium sulphate . . . . . . 1·3156 grm.
Calcium oxide . . . . 0·3295 grm.

Hence 1·3156 × 0·2403 = 0·3161 grm. CaO; and 0·3295 - 0·3161 = 0·0134 grm. CaO. Consequently the sample has 0·0134 × 1·7847 = 0·0239 grm. CaCO₃; and 1·3156 × 0·5832 = 0·7673 grm. CaSO₄.

§ 292. The Analysis of Barytes and Witherite.

Barytes, heavy spar or barite is a variety of native barium sulphate and witherite a native barium carbonate. These minerals are so cheap that they are very seldom adulterated and the analysis is therefore directed to the determination of the natural impurities.[1] The minerals are often found in commerce ground to impalpable powders. The analysis may involve the determination of barium and calcium sulphates, barium and calcium carbonates, magnesia, silica, alumina, ferric oxide and moisture. This latter is determined by drying about 2 grms. at 110° for a couple of hours. Traces of lead, copper and zinc are sometimes present. Fluorides (fluorspar) are not at all uncommon. A high-grade sample of barytes may run:

BaSO₄	SiO₂	Al₂O₃	Fe₂O₃	MgCO₃	CaCO₃	H₂O
96·5	0·5	0·5	0·2	0·2	1·2	0·5

Barium Sulphate and Silica.—Boil a gram of the sample in dilute hydrochloric acid (1 : 3) and evaporate the solution to dryness. Moisten the mass with dilute acid, digest with water, boil, filter, wash. The filtrate contains iron oxide, alumina, lime and magnesia[2]; the insoluble residue contains barium sulphate and "silica." Ignite and weigh in a platinum crucible[3] as "total insoluble."[4] This is sometimes reckoned as barium sulphate. To correct the "total insoluble" for silica, add sulphuric and hydrofluoric acids. Evaporate to dryness, ignite and weigh. The loss in weight represents silica.

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[1] J. Aron, *Notizblatt*, 8, 293, 1872; E. S. Hertzog, *Ind. Eng. Chem. Anal. Ed.*, 9, 336, 1937.

[2] Barium carbonate, if present, is also dissolved. The barium chloride can be removed from the filtrate by the addition of dilute sulphuric acid (page 582) and reported as barium carbonate.

[3] Assuming that the qualitative analysis has shown the absence of lead.

[4] Some prefer to fuse the insoluble matter with sodium carbonate. Take up the mass with water, etc., as described below.

The alumina, ferric oxide, lime and magnesia are determined in the filtrate in the usual way.

Soluble Sulphate.—Boil 1 grm. of the powdered sample with 20 c.c. of concentrated hydrochloric acid, add 200 c.c. of hot water, boil, filter and wash. Determine the sulphates in the filtrate by the addition of barium chloride (page 703). Multiply the weight of the barium sulphate obtained by 0·5832 to get the corresponding amount of calcium sulphate and by 0·2403 to get the corresponding amount of CaO. If the amount of CaO so determined be less than that obtained by the oxalate process, and if carbonates are present, report the equivalent of the remaining calcium oxide as calcium carbonate; and if carbonates are absent, report the remaining CaO as lime.

Loss on Ignition.—On ignition of a given sample in a platinum crucible, the loss in weight represents water (free or combined with gypsum or clay), carbon dioxide from the whiting and organic matter.

Complete Analysis.—A more exact analysis can be made by fusing a couple of grams of the sample with sodium carbonate in a platinum crucible.[1] Digest the fused mass with hot water [2] until the alkali sulphates and carbonates are all dissolved. Filter the hot solution and wash the insoluble residue with water. A slight excess of hydrochloric acid is added to the filtrate, which is then evaporated to dryness. The silica is removed by evaporation in the usual way; and sulphuric acid is determined in the filtrate by the method of page 703. The excess of barium, used in the precipitation of the sulphuric acid, is now removed from the filtrate by the process of § 286, page 582. The precipitated barium sulphate is filtered off, washed and the filtrate alone retained. The insoluble residue is dissolved in dilute hydrochloric acid, evaporated to dryness and the silica retained by it separated as usual. In the filtrate from the silica, the barium is precipitated as above and weighed as sulphate. The filtrates from the two respective precipitations of barium sulphate are then combined—aluminium and ferric hydroxides are precipitated by the addition of ammonia (page 164) and the calcium determined in the filtrate by the oxalate process.

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[1] According to E. R. Caley (*Journ. Amer. Chem. Soc.*, **55**, 3947, 1933), all difficultly soluble sulphates can be decomposed by digestion with hot, concentrated hydriodic acid. The apparent reactions are: $BaSO_4 + 8HI = BaS + 4H_2O + 4I_2$ and $BaS + 2HI = BaI_2 + H_2S$.

[2] Note, if hydrochloric acid be used for the extraction, insoluble barium sulphate is re-formed. During the fusion: $BaSO_4 + Na_2CO_3 = BaCO_3 + Na_2SO_4$. The latter is soluble in water; the barium carbonate is insoluble. If hydrochloric acid be used, barium carbonate dissolves and barium sulphate is reprecipitated by the soluble sulphate.

CHAPTER XXXVII.

SPECIAL METHODS FOR THE DETERMINATION OF ALKALIES AND THEIR SALTS.

§ 293. The Gravimetric Determination of Lithium—Kahlenberg's Process.

LITHIUM can be detected in many clays and in most natural silicates by means of the spectroscope,[1] but it is usually present in such small quantities in clays that a quantitative separation is impracticable. Some samples of Cornish stone, however, may have appreciable amounts of lithium.[2] It is generally stated that the lithium will be found in the ordinary course of analysis, mixed with the chlorides of potassium and sodium.[3] As a matter of fact, lithium carbonate may be precipitated when a solution of lithium chloride is treated with an alkali carbonate, for 100 c.c. of water, at 15°, dissolve but 1·36 grms., and 100 c.c. of alcohol (sp. gr. 0·941), 0·06 grm. of the carbonate.[4] The solubility is, however, much increased in the presence of ammonium salts, so that no precipitate will be obtained if a sufficient excess of these salts be present. Again, when calcium is precipitated as oxalate, lithium is retained so tenaciously that it is exceedingly difficult to wash the lithium from the precipitate. This uncertainty about the location of the lithium salts makes it desirable to proceed a little differently from the method indicated on page 216, when lithium is to be determined.

The Isolation of Lithium Salts.—After treating the sintered cake formed during the ignition, in Smith's process (page 215), with water, the aqueous extract is evaporated to dryness in a platinum dish with the occasional addition of concentrated hydrochloric acid. Dry at 110° for about half an hour. Extract the residue with 25 c.c. of 95 per cent. alcohol, and wash it with alcohol

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[1] Compare W. O. Robinson, L. A. Steinkoenig and C. F. Miller, *U.S. Dept. Agr. Bull.*, 600, 1917.

[2] The separation of alumina in the analysis of lithium silicates—according to K. and E. Sponholz (*Zeit. anal. Chem.*, 31, 521, 1892)—requires four or five precipitations of the alumina with ammonia to get the alumina free from lithium. The basic acetate separation, however, is said to present no particular difficulty.

[3] Along with rubidium and cæsium chlorides—A. A. Anderson, *Min. Eng. World*, 36, 1055, 1912. For the contamination of potassium chloroplatinate with lithium, see G. Jenzsch, *Pogg. Ann.*, 104, 102, 1858. For the possible loss of rubidium and cæsium salts during fusion with alkali carbonates, see N. M. von Wittorf, *Zeit. anorg. Chem.*, 39, 187, 1904.

[4] J. Bevade, *Bull. Soc. chim.*, (2), 43, 123, 1885; F. Ageno and E. Valla, *Atti Accad. Lincei*, (5), 20, ii, 706, 1911; P. A. Flückiger, *Arch. Pharm.*, (3), 25, 542, 1887; C. N. Draper, *Chem. News*, 55, 169, 1887; G. Geffeken, *Zeit. anorg. Chem.*, 43, 197, 1905. At 25° the solubility of lithium carbonate in water is about 0·34 grm. equivalent per litre; the solubility is not much affected by alkali chlorides or nitrates; it is slightly augmented by alkali sulphates and considerably augmented by ammonium salts—thus, in 0·25N-ammonium sulphate the solubility number is 0·51, and with 2N-solutions 1·17.

until the lithium is all removed.[1]　Evaporate the filtrate and washings to dryness [2] along with a little hydrochloric acid.　The residue is now extracted with absolute alcohol until the runnings are free from lithium.　Evaporate to dryness as before and treat the residue with a little dilute hydrochloric acid. Make the solution alkaline with calcium hydroxide[3] and filter off the precipitated magnesium hydroxide.[4]　Precipitate the lime with ammonia and ammonium oxalate in the usual way.　Filter and thoroughly wash with water— 100 c.c. usually suffice to free the precipitate from lithium.　Evaporate the filtrate to dryness, drive off the ammonium salts and repeat the treatment with dilute acid, ammonia and ammonium oxalate.　After evaporation to dryness as before, the residue containing the lithium chloride, along with traces of potassium and sodium chlorides,[5] is treated by the pyridine or the amyl alcohol process.

Fig. 119.—Solubility of Lithium Chloride in Pyridine.

The Solubility of Lithium Chloride in Pyridine. - - The separation of lithium from a mixture of alkali chlorides is based on the fact that the chlorides of sodium and potassium [6] are practically insoluble in solutions of pyridine containing less than 3 per cent. of water.　Lithium chloride is fairly soluble in anhydrous as well as in aqueous

[1] Lithium may be detected spectroscopically in the residue when it is present in unweighably small amounts.　A small direct-vision spectroscope with a slit will show a crimson lithium band between the yellow sodium line and the red potassium line (Plate II.).　The spectra of the alkalies are shown on Plate II.　The spectroscopic method will detect $\frac{1}{5,000,000}$ mgrm. of soda; $\frac{1}{1000}$ mgrm. of potash; $\frac{1}{1,000,000}$ mgrm. lithia; $\frac{1}{500}$ mgrm. rubidia (Bunsen). For the spectrometric method of determining lithium, see G. Ranzoli, *Gazz. Chim. Ital.*, 31, i, 40, 1901; M. Curie and E. Gleditsch, *Compt. rend.*, 147, 345, 1908; L. A. Steinkoenig, *Journ. Ind. Eng. Chem.*, 7, 425, 1915; W. W. Skinner and W. D. Collins, *Eighth Inter. Cong. App. Chem.*, 1, 453, 1912; A. P. Snesarev, *Journ. prakt. Chem.*, (2), 141, 327, 1934.

[2] Recover alcohol in the usual way.

[3] L. R. Milford, *Journ. Ind. Eng. Chem.*, 4, 595, 1912.　The use of lime water instead of baryta water for precipitating magnesium avoids introducing a foreign substance.　Calcium is already present and calcium oxalate is less soluble and more easily washed than barium oxalate.

[4] J. D. Dinwiddie (*Amer. Journ. Sci.*, (4), 39, 662, 1915) uses alcoholic ammonium carbonate to separate magnesium from lithium.　L. Moser and K. Schutt (*Monats.*, 51, 53, 1929) say that 8-hydroxyquinoline is more satisfactory.

[5] If iodides or bromides were present, they would be found with these chlorides, since the bromides and iodides are more soluble than chlorides.　In that case, an evaporation to dryness with hydrochloric acid and chlorine water, followed by a gentle ignition, will ensure a residue consisting of chlorides only—L. R. Milford (*l.c.*).

[6] Also rubidium and cæsium.　According to M. Sérullas (*Ann. Chim. Phys.*, (2), 46, 294, 1831), perchloric acid does not precipitate lithium perchlorate from concentrated solutions of lithium chloride.　For the solubilities of alkali perchlorates in organic solvents and the separation of lithium from potassium and sodium perchlorates, see G. F. Smith, *Journ. Amer. Chem. Soc.*, 47, 762, 1925; G. F. Smith and J. F. Ross, *ib.*, 47, 1020, 1925; H. H. Willard and G. F. Smith, *ib.*, 44, 2816, 1922; L. Moser and K. Schutt, *Monats.*, 51, 53, 1929.

PLATE II.

Chemical Analysis. J. W. Mellor, D. Sc. London, Charles Griffin & Co., Ltd.

SPECTRA OF ALKALI METALS (WITH FRAUNHOFER'S LINES OF SOLAR SPECTRUM AS STANDARDS OF REFERENCE.)

solutions of pyridine.[1] The solubility of lithium chloride in anhydrous and in 97 per cent. pyridine solutions at different temperatures is shown in the diagram, fig. 119. The curious break in the curve with anhydrous pyridine is supposed to be due to the fact that below 28° the solution contains $LiCl.2C_5H_5N$, and above 28°, $LiCl.C_5H_5N$.

The graph shows that at 20°, 100 grms. of anhydrous pyridine dissolve 13·39 grms. of lithium chloride, and 100 grms. of the 97 per cent. pyridine (97 vols. anhydrous pyridine, 3 vols. water) at 22° dissolve 14·31 grms. of lithium chloride. Kahlenberg and Krauskoff have based upon these facts a process for the separation of lithium chloride from the other alkali chlorides.

1. *First Extraction.*—Evaporate the aqueous solution of the mixed chlorides[2] to dryness. Add a couple of drops of hydrochloric acid.[3] Evaporate the mass again to dryness. Digest the residue with about 25 c.c. of boiling anhydrous pyridine[4] for 5 or 10 minutes. Break up any large masses with a stirring-rod with a rounded end. Let the insoluble residue settle. Decant the clear liquid through a small filter-paper — 7·0 cm. Collect the filtrate in a small Erlenmeyer's flask and wash the residue with about 5 c.c. of hot pyridine.

2. *Second Extraction.* — Lithium chloride is retained with great tenacity by the insoluble alkali chlorides and a second extraction is therefore necessary. Dissolve the
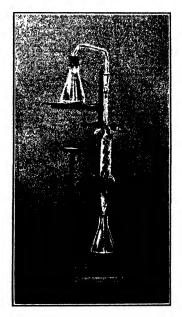
Fig. 120.—The Recovery of Pyridine.

residue in a small amount of water with a drop of hydrochloric acid. Evaporate the solution to dryness and repeat the extraction with hot pyridine.[5] Combine the filtrates and washings from the different extractions. Distil off the pyridine by connecting the Erlenmeyer's flask with a small condenser (fig. 120). When the residue in the flask is nearly dry, let the mass cool.

3. *Transformation of Lithium Chloride to Lithium Sulphate.*— Dissolve the mass in water acidulated with sulphuric acid in order to transform the lithium chloride into lithium sulphate. Filter off any organic residue which may be present, and collect the filtrate in a weighed platinum dish. Evaporate to dryness. Drive off the excess of sulphuric acid at a gentle heat.[6] Fuse and weigh. Multiply the weight of the lithium sulphate so obtained by 0·27178 to get the corresponding amount of lithia—Li_2O.

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[1] A. Neumann and J. Schroeder, *Ber.*, 37, 4609, 1904; L. Kahlenberg, *Journ. Amer. Chem. Soc.*, 24, 401, 1902; L. Kahlenberg and F. C. Krauskoff, *ib.*, 30, 1104, 1908; E. Murmann, *Zeit. anal. Chem.*, 50, 171, 273, 1911. Compare L. Moser and K. Schutt, *Monats.*, 51, 53, 1929.

[2] Weighing less than 0·2 grm.

[3] In order to convert any lithium hydroxide into chloride. The hydroxide is formed by hydrolysis of the chloride and it is not so soluble in the pyridine.

[4] The purest pyridine should be used for this purpose. The cheaper material should be purified by distillation from fused potash and the fraction boiling between 114° and 116° be used for the work.

[5] If a relatively large amount of other alkali chlorides and a relatively small amount of lithium chloride be present, a third extraction may be advisable.

[6] According to I. Kitajama (*Journ. Chem. Soc. Japan*, 55, 199, 1934), the ignition temperature should not be less than 470°.

In illustration of the excellent results which may be obtained by this process, the following experiments with artificial mixtures of lithium chloride with potassium, sodium and barium chlorides are reported:—

Table LVIII.—Test Analyses for Lithium.

Lithium chloride.		Residue.		Besides lithium chloride, the mixture contained, in grms.:—
Used. Grm.	Found. Grm.	Used. Grm.	Found. Grm.	
0·0958	0·0956	0·6007	0·6001	0·2020 KCl ; 0·3082 NaCl ; 0·0905 BaCl₂
0·0907	0·0903	0·5867	0·5863	0·1933 KCl ; 0·2913 NaCl : 0·1021 BaCl₂

The Determination of the Potassium and Sodium Chlorides.—If the mixture of alkali chlorides of J. L. Smith's process has been under treatment, the residues on the filter-papers which have been washed by the 95 per cent. and the absolute alcohol, as well as all the other succeeding residues, are collected together, dissolved in water and treated as indicated on page 221 *et seq.*, for potassium and sodium.

A marked objection to this process is the unpleasant smell of the pyridine, hence the work should be done under a well-ventilated hood. The use of pyridine is eliminated in Gooch's process which, nowadays, is the more favoured method for determining lithium.

§ 294. The Gravimetric Determination of Lithium— Gooch's Process.

Gooch's process[1] is based upon the fact that lithium chloride is soluble in amyl alcohol—10 c.c. dissolve 0·75 grm. of lithium chloride—whereas sodium and potassium chlorides are but sparingly soluble in the same menstruum.[2] Gooch has shown that 10 c.c. of the alcohol dissolve 0·00041 grm. of sodium chloride and 0·00051 grm. of potassium chloride. Hence, if a mixture of lithium, potassium and sodium chlorides be washed with amyl alcohol, lithium chloride will be removed, while sodium and potassium chlorides remain behind as sparingly soluble residues.

Winkler[3] recommends the use of isobutyl alcohol instead of amyl alcohol on hygienic grounds and also for the reason that 10 c.c. of isobutyl alcohol dissolve

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[1] F. A. Gooch, *Proc. Amer. Acad.*, **22**, 177, 1886; *Amer. Chem. Journ.*, **9**, 33, 1887; *Chem. News*, **55**, 18, 29, 40, 56, 78, 1887; E. Waller, *ib.*, **62**, 173, 181, 1890; *Journ. Amer. Chem. Soc.*, **12**, 214, 1890; W. J. Schieffelin and W. R. Lamar, *ib.*, **24**, 392, 1902; E. R. Caley, *ib.*, **52**, 2754, 1930; H. Yagoda, *ib.*, **54**, 984, 1932; B. Feigenberg, *Eine neue Trennungsmethode des Lithiums von anderen Alkalimetallen*, Berlin, 1905; A. A. Anderson, *Min. Eng. World*, **36**, 1055, 1912; W. W. Skinner and W. D. Collins, *Bull. U.S. Dept. Agric. Chem.*, **153**, 1, 1912; E. Schürmann and W. Böhm, *Chem. Ztg.*, **50**, 709, 1926; **51**, 677, 698, 1927.

[2] Rubidium and cæsium chlorides are also practically insoluble in the same solvent—less than 0·0009 grm. is dissolved by 10 c.c. of hot amyl alcohol.

[3] L. W. Winkler, *Zeit. anal. Chem.*, **52**, 628, 1913; L. Moser and K. Schutt, *Monats.*, **51**, 53, 1929. The latter state that the mixed chlorides should be dried at 120°–150° and then extracted with isobutyl alcohol which has been dehydrated by repeated refluxing with barium oxide.

only 0·0005 grm. of other alkalies, weighed as sulphates.   The correction (see page 604) is thus somewhat reduced.   Other organic solvents have been advocated.[1]

The Separation.—The mixed chlorides—say, 0·2 grm.[2] or less—are dissolved in water and filtered into a 50–80 c.c. Erlenmeyer's flask.   Evaporate the
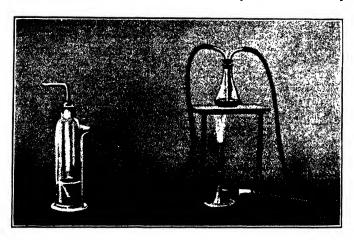
FIG. 121.—Removal of Water from Amyl Alcohol.

solution slowly on an asbestos pad over a small flame until the salts show signs of crystallising (1–2 c.c.).   Add a couple of drops of water and a couple of drops of concentrated hydrochloric acid.   Treat the concentrated solution of the mixed chlorides so obtained with 10–15 c.c. amyl alcohol (boiling-point, 129°–132°) in the Erlenmeyer's flask (fig. 121), fitted with a cork through which passes a capillary tube dipping in the liquid, and also another tube connected to an aspirator.   The free end of the capillary tube is then connected to a wash bottle charged with concentrated sulphuric acid.   The flask is heated on an asbestos plate to the boiling-point while a current of air is slowly aspirated through the liquid.   This prevents any violent bumping of the alcohol and facilitates the escape of water vapour through the upper layer of amyl alcohol. When the water and about half the amyl alcohol have boiled off, the chlorides of sodium and potassium and a little lithium hydroxide[3] are deposited, while the lithium chloride remains in solution in the alcohol.   Let the liquid cool; add two or three drops of concentrated hydrochloric acid in order to transform the lithium hydroxide into chloride.   Heat the contents of the flask to the

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[1] For a mixture of alcohol and ether, see S. Palkin, *Journ. Amer. Chem. Soc.*, **38**, 2326, 1916; for acetone, M. H. Brown and J. H. Reedy, *Ind. Eng. Chem. Anal. Ed.*, **2**, 304, 1930; R. C. Wells and R. E. Stevens, *ib.*, **6**, 439, 1934; for diethylene dioxide (dioxane), A. Sinka, *Zeit. anal. Chem.*, **80**, 430, 1930; for amyl alcohol and pyridine, J. Bardet, A. Tchakirian and R. Lagrange, *Compt. rend.*, **204**, 443, 1937.

[2] If more than this amount of the mixed chlorides be present, concentrate the lithia by digesting the mixed chlorides with 25 c.c. of a mixture of equal volumes of anhydrous alcohol and ether for about an hour in a corked flask.   The ether should have been distilled from quicklime, otherwise the concentration of the lithium is not effected.   Some lithium hydroxide remains in the residue.   Hydrochloric acid is usually added to retard the hydrolysis of the chloride.

[3] Formed by the hydrolysis of the chloride.   Lithium hydroxide is but sparingly soluble in amyl alcohol.

boiling-point and let the whole stand half a minute while aspirating a current of air through the fluid. Filter the hot liquid through a Gooch crucible packed with asbestos. The volume of the *hot* alcohol which has been in contact with the undissolved chlorides is measured. Wash the precipitate and flask with *cold* amyl alcohol, which has been boiled to remove moisture, until the filtrate shows no trace of lithia. When the amount of lithium chloride exceeds 10–20 mgrms. it is advisable to redissolve the precipitate in a little water and repeat the treatment. Evaporate the filtrates and washings to dryness in an air bath at a temperature not exceeding 125°.[1] Dissolve the residue in a little water acidulated with sulphuric acid. Filter off the organic residue. Collect the filtrate in a weighed platinum dish, evaporate on a water bath and drive off the excess of sulphuric acid at a gentle heat. Calcine the lithium sulphate in the platinum dish to make sure all the carbon left by the amyl alcohol is burnt. The sulphate is fused one minute. When the dish is partly cooled, cover it with a watch-glass to return any fragments of lithium sulphate which may spit off as the cooling mass contracts. Cool in a desiccator and weigh; again heat the dish up to the fusion-point of the sulphate, cool as before and weigh. The weight is usually constant. Multiply the weight of lithium sulphate so obtained by 0·27178 to get the corresponding amount of Li_2O.

Corrections.—A deduction must be made for the potassium and sodium chlorides dissolved by the boiling amyl alcohol in contact with the mixed chlorides. The potassium and sodium chlorides dissolved by the cold amyl alcohol used in the washings are neglected. Subtract 0·00050 grm. from the weight of lithium sulphate for every 10 c.c. of amyl alcohol in the filtrate, *exclusive of washings*, if the lithium is being separated from sodium chloride, 0·00059 grm. if the lithium is being separated from potassium chloride and 0·00109 grm. if the lithium is being separated from both sodium and potassium chlorides.

Determination of the Sodium and Potassium Chlorides.—Dissolve the mixed chlorides in the Gooch crucible in water, evaporate the solution to dryness in a weighed porcelain dish and weigh. Separate the two chlorides as indicated on page 224. If lithium and sodium are alone being treated, add 0·00041 grm. to the weight of the sodium chloride for every 10 c.c. of amyl alcohol used in the actual extraction, *exclusive of washings*, 0·00051 grm. to the potassium chloride, if potassium and lithium chlorides are being treated, and 0·00092 grm. if the three chlorides—sodium, potassium and lithium—are in question.

Errors.—Duplicates with this process agree very well. The chief errors arise from those incidental to Smith's process (page 214), as well as (1) bumping when driving off the amyl alcohol; (2) filtering the amyl alcohol solutions hot; (3) neglect to evaporate the amyl alcohol in the dish at a temperature below the boiling-point of amyl alcohol; (4) foaming or spurting when driving off the sulphuric acid from the lithium sulphate; and (5) neglect to protect the dish when the lithium sulphate is cooling. A lithium determination by this process, starting from the dry silicate, occupies about two days.[2]

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[1] The amyl alcohol rapidly evaporates at this temperature without loss of lithium by spattering.

[2] For the determination of lithium as stearate, see E. R. Caley, *Journ. Amer. Chem. Soc.*, 52, 2754, 1930; as phosphate, B. Brauner, *Coll. Czech. Chem. Comm.*, 2, 442, 1930; as arsenate, T. Gaspar, *Ann. Fis. Quim.*, 30, 406, 1932; as chloride (indirect method), S. D. Averitt, *Journ. Ind. Eng. Chem.*, 9, 584, 1917. C. C. Miller and F. Traves (*Journ. Chem. Soc.*, 1395, 1936), after extraction by amyl alcohol or acetone, precipitate the lithium as the triple acetate, $LiZn(UO_2)_3(CH_3COO)_9.6H_2O$.

§ 295. The Evaluation of Potassium and Sodium Salts.

Sodium Nitrate—Chili Saltpetre.

Sodium nitrate or Chili saltpetre usually contains between 95 and 98 per cent. sodium nitrate.[1] The general impurities are potassium nitrate (up to 9 per cent. in extreme cases),[2] sodium chloride, sodium sulphate, sodium iodate,[3] sodium perchlorate,[4] sodium carbonate (rare), magnesium sulphate (rare), calcium salts and insoluble matter. A common method of evaluating the salt is to determine the percentage moisture, sodium chloride, sodium sulphate and insoluble matter. These are grouped together as the "refraction," and the remainder is supposed to be sodium nitrate. There are many objections to this process, more particularly if the salt is to be used in the manufacture of nitric acid. Thus potassium nitrate may be present and this would interfere with the calculated yield of acid from the nitrate. The only reliable procedure is to determine the amount of nitrate present in the sample [5] (*v. infra*).

Determination of Moisture and Insoluble Matter.— For the determination of the moisture, heat 10 grms. of the nitrate in an air bath at 120°-130° until the weight is constant. This takes about two hours. The insoluble matter is determined by digesting 50 grms. of the salt in water and filtering the solution through a tared filter-paper or Gooch crucible, in the usual manner.

Determination of Calcium, Magnesium and Iron ; Chlorides and Sulphates.— Place 20 grms. of the sample in a filter-paper resting in a funnel in the neck of a litre flask. Pour boiling distilled water through the paper. When the solution is cold, make it up to the mark on the neck of the flask with cold distilled water. Pipette 50 c.c. for the determination of chlorides gravimetrically (page 746) or volumetrically (pages 65, 68). Another 50 c.c. are treated with barium chloride and the barium sulphate determined in the usual manner (page 703). The lime is determined in 200 c.c. by precipitation as calcium oxalate (page 203) and the magnesia is determined in the filtrate from the calcium oxalate by precipitation as phosphate (page 208). Iron can be determined colorimetrically (page 185) or, if in appreciable quantity, by precipitation with ammonia, prior to the determination of calcium (page 164).

Determination of Sodium Carbonate.—The presence of carbonates can be detected by the test given on page 623. If, and when, the amount of sodium carbonate is required, 200 c.c. of the solution, prepared as above, are titrated with 0·1N-sulphuric or hydrochloric acid, using methyl orange as indicator.[6]

[1] R. Alberti and W. Hempel, *Zeit. angew. Chem.*, 5, 101, 1892.

[2] G. Lunge, *Chem. Ind.*, 9, 269, 1886; H. Hagen, *Chem. Ztg.*, 15, 1528, 1891; *Zeit. angew. Chem.*, 6, 495, 698, 1893.

[3] H. Beckurts, *Pharm. Centralhalle*, 233, 1886.

[4] H. Beckurts, *Archiv Pharm.*, 224, 333, 1886; H. Fresenius and H. Bayerlein, *Zeit. anal. Chem.*, 37, 501, 1898. For the determination of perchlorates in nitrates, see F. Winteler, *Chem. Ztg.*, 21, 75, 1897; O. Förster, *ib.*, 22, 357, 1898; D. Tschernobéev, *ib.*, 29, 442, 1905; A. Wogrinz and J. Kuber, *ib.*, 43, 21, 1919; H. Lemaître, *Mon. Sci.*, (4), 18, 253, 1904; *Chem. Centr.*, (1), 1427, 1904; W. S. Hendrixson, *Amer. Chem. Journ.*, 32, 242, 1904; A. Monnier, *Arch. Sci. phys. nat.*, (4), 42, 210, 1916; K. A. Hofmann, F. Hartmann and U. Hoffmann, *Ber.*, 58B, 2748, 1925; F. L. Hahn, *Zeit. angew. Chem.*, 39, 451, 1926; O. S. Fedorova, *Journ. Russ. Phys. Chem. Soc.*, 59, 265, 1927.

[5] W. S. Allen, *Eighth Inter. Cong. App. Chem.*, 1, 19, 1912; N. Busvold, *Chem. Ztg.*, 38, 799, 1914; E. R. Allen, *Journ. Ind. Eng. Chem.*, 7, 521, 1915; C. A. Butt, *ib.*, 12, 352, 1920.

[6] Calcium, if present, will be precipitated by the sodium carbonate, thus reducing the amount of the latter, as reported from the titration. The total carbonates in the sample can be determined by the method given for whiting, page 58.

If the volume of acid used be v c.c., then the percentage of sodium carbonate in the sample is $0.53\ v/4$.

Determination of Potassium.—The potassium is determined by dissolving half a gram of the salt in an Erlenmeyer's flask in 25 c.c. of dilute hydrochloric acid. Filter, heat the solution to boiling and add just sufficient barium chloride, drop by drop, to precipitate the sulphates as barium sulphate. Wait after each addition until the supernatant liquid is clear, and add the barium chloride until a drop ceases to produce a cloudiness. Remove the excess of barium and any calcium which may be present by the procedure indicated on page 217. The potassium is determined in the final residue of alkali salts by the perchlorate process (page 224). See also page 608.[1]

Determination of Nitrates.—Connect a round-bottomed flask of about 1000 c.c. capacity through an efficient splash head with a reflux condenser (fig. 120), using rubber bungs[2] for all connections. Immerse the lower end of the condenser tube beneath the surface of 50 c.c. of $0.2N$-sulphuric acid, contained in an Erlenmeyer's flask. Pipette into the litre flask 25 c.c. of the stock nitrate solution, prepared from 20 grms. of the sample as indicated on page 605. Dilute with water to about 300 c.c., add 5 c.c. of alcohol, 2 grms. of Devarda's alloy[3] and 20 c.c. of a 25 per cent. solution of sodium hydroxide. Immediately connect the flask again to the splash head and stand for about an hour, during which time the greater bulk of the nitrate will have been reduced to ammonia. Then carefully heat the flask until the alloy has been completely decomposed and finally boil gently for about 30 minutes to expel all the ammonia. Before turning off the heat disconnect the condenser from the splash head. Raise the condenser out of contact with the acid liquid in the Erlenmeyer's flask and then well rinse the inside and end of the condenser, collecting the washings in the flask. Titrate the whole of the liquid in the flask with $0.2N$-sodium hydroxide, using methyl orange as indicator.

CALCULATION.—The difference between the volume of $0.2N$-acid taken and the volume of $0.2N$-alkali used in the back-titration gives the volume, v, of $0.2N$-acid neutralised by the ammonia, produced on reduction of the nitrates in 0.5 grm. (*i.e.* 25 c.c. of the stock solution) of the sample, according to the equation: $NaNO_3 + 4H_2 = NaOH + NH_3 + 2H_2O$. Hence $200\ v$ c.c. of $0.2N$-acid will be needed to neutralise the ammonia obtained from 100 grms. of the sample. But this volume of acid will neutralise $200\ v$ c.c. of $0.2N$-ammonia, which, in turn, will be produced from $200\ v$ c.c. of $0.2N$-sodium nitrate solution or $200\ v \times 0.017 = 3.4\ v$ grms. of $NaNO_3$. To report in terms of potassium nitrate multiply by 1.1894.

Potassium Nitrate—Saltpetre, Nitre.

The moisture is determined as in the case of sodium nitrate. Less than 0.25 per cent. of moisture is usually present. For the chlorine, dissolve 100 grms. of the salt in water, filter and wash with hot water. The solution is treated with silver nitrate and the chlorine determined by the turbidity method or gravimetrically. Less than 0.01 per cent. is usually present. The insoluble matter, sulphates, lime and magnesia are determined as in the case of sodium nitrate. The sodium is determined as indicated on page 235.

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[1] Compare W. Vaubel, *Zeit. öffentl. Chem.*, **20**, 426, 1914; **21**, 1, 1915.
[2] Or ground glass joints.
[3] Aluminium, 45 per cent.; copper, 50 per cent.; zinc, 5 per cent.—A. Devarda, *Chem. Ztg.*, **16**, 1952, 1892.

Potassium Carbonate—Pearl Ash.

The moisture and insoluble matter are determined as just indicated for sodium nitrate. The available alkali is determined by titration as on page 57. The chlorides, sulphates, insoluble matter, silicates and phosphates are determined in the usual way. Iron is determined colorimetrically. The total potassium is determined as indicated under sodium nitrate. The results are expressed by calculating the amount of potassium chloride from the silver chloride and the amount of potassium sulphate from the amount of barium sulphate. Then calculate the amount of potassium carbonate from the difference between the total potash and that corresponding with the potassium chloride and sulphate. Calculate the amount of sodium carbonate from the difference between the available alkali and the potassium carbonate calculated as indicated above. For a further discussion on sodium and potassium carbonates, see page 60.

§ 296. The Determination of Potassium Colorimetrically— Cameron and Failyer's Process.

When potassium chloroplatinate is dissolved in water and mixed with an excess of a solution of potassium iodide, the intensity of the red colour so obtained is proportional to the amount of potassium chloroplatinate [1] in the solution. This reaction may therefore be used quantitatively for the determination of very small quantities of potassium. Ammonium chloroplatinate produces a similar coloration and therefore all the reagents, also the atmosphere of the laboratory in which the determination is made, must be free from ammonia.

Standard Solution.—Dilute 10 c.c. of standard potassium chloroplatinate solution [2] to about 30 c.c.; add a drop of hydrochloric acid (1 : 1) and 0·5 c.c. of potassium iodide solution.[3] Let the mixture stand for about an hour to permit the colour to develop fully and then dilute to 100 c.c. The colour of the test solution is developed at the same time.

Test Solution.—The potassium chloroplatinate is isolated as indicated on page 231.[4] The salt is collected on the asbestos felt [5] of a Gooch crucible rather than on filter-paper, because of the difficulty in getting filter-paper quite free from ammonia. The dried precipitate of potassium chloroplatinate is dissolved in hot water by washing the crucible until about 25 c.c. of filtrate have been obtained. Cool the filtrate; add a drop of hydrochloric acid, and 0·5 c.c. of potassium iodide solution. After the solution has stood for an hour, dilute to 100 c.c. The comparison is made in the usual way.[6]

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[1] F. K. Cameron and G. H. Failyer, *Journ. Amer. Chem. Soc.*, **25**, 1063, 1903; L. A. Hall, *ib.*, **25**, 990, 1903; T. T. Morrell, *ib.*, **2**, 145, 1880; O. Schreiner and G. H. Failyer, *Bull. U.S. Dept. Agric.* (Soils), **31**, 31, 1906.

[2] STANDARD POTASSIUM CHLOROPLATINATE SOLUTION.—Dissolve 0·0484 grm. of carefully recrystallised potassium chloroplatinate—K_2PtCl_6—in water and dilute the solution to a litre. Each c.c. of this solution is equivalent to 0·00001 grm. of K_2O.

[3] POTASSIUM IODIDE SOLUTION.—Dissolve 25 grms. of potassium iodide in water and make the solution up to 100 c.c.

[4] Special care must be taken to make sure all the ammonium salts are driven off during the ignition of the mixed chlorides.

[5] The asbestos is washed (page 92), and ignited in a platinum dish to remove all traces of ammonia. Preserve the asbestos in alcohol in a well-stoppered bottle.

[6] Whichever solution is the stronger, dilute it still more, or take an aliquot portion and dilute it to 100 c.c.

§ 297. Colorimetric Cobaltinitrite Process.

In other and more modern methods, the potassium is precipitated as cobaltinitrite (see § 298) and the amount of nitrite in the precipitate is determined colorimetrically by the production of a dye through the interaction of the nitrous acid of the nitrite with suitable organic reagents.[1] The accuracy of these processes depends primarily on the constancy in composition of the precipitated cobaltinitrite.

§ 298. The Determination of Potassium—Cobaltinitrite Process.

A solution of sodium cobaltinitrite, $Na_3Co(NO_2)_6$ – also called Koninck's reagent—precipitates canary-yellow potassium sodium cobaltinitrite when added to a solution of a potassium salt.[2] The corresponding salts of lithium, magnesium, strontium, calcium, iron, aluminium and zinc are soluble and hence potassium salts can be readily detected in the presence of these compounds. Cæsium, rubidium and ammonium[3] salts, like potassium salts, give sparingly soluble cobaltinitrites. The reaction proceeds in the presence of chlorides, sulphates, nitrates, phosphates and acetates. The reaction is quantitative so far as the separation of potassium from sodium is concerned,[4]

[1] E. Riegler, *Zeit. anal. Chem.*, **36**, 377, 1897; M. von Wrangell and H. Beutelspacher, *ib.*, **90**, 401, 1932; S. N. Rozanov and V. A. Kazarinova, *ib.*, **96**, 26, 1934; J. Tischer, *Biochem. Zeit.*, **238**, 148, 1931; R. A. Herzner, *ib.*, **237**, 129, 1931; F. Alten, H. Weiland and B. Kurmies, *Zeit. Pflanz. Düng. Bodenk.*, **32A**, 171, 1933; J. Tisher, *ib.*, **33A**, 335, 1934. See also E. M Emmert, *Journ. Assoc. Off. Agric. Chem.*, **14**, 573, 1931; G. V. Prikhodko, *Journ. App. Chem. (U.S.S.R.)*, **5**, 99, 1932; F. Lebermann, *Klin. Wochschr.*, **3**, 1632, 1924; *Biochem. Zeit.*, **150**, 548, 1924; J. Tischer, *Mikrochem., H. Molisch Festschrift*, 418, 1936; C. P. Sideris, *Ind. Eng. Chem. Anal. Ed.*, **9**, 145, 1937. For the colorimetric determination of potassium as picrate, see E. R. Caley, *Journ. Amer. Chem. Soc.*, **53**, 539, 1931; I. N. Antipov-Karataev and A. M. Myasnikova, *Proc. Leningrad Dept. Inst. Fert.*, **17**, 81, 1933. Compare A. Bolliger, *Journ. Biol. Chem.*, **107**, 229, 1934.
[2] O. L. Erdmann, *Journ. prakt. Chem.*, (1), **97**, 385, 1866; G. P. Sadtler, *Amer. J. Science*, (2), **49**, 189, 1870; L. L. de Koninck, *Zeit. anal. Chem.*, **20**, 390, 1881; E. Bjilmann, *ib.*, **39**, 284, 1900; C. O. Curtmann, *Ber.*, **14**, 1951, 2121, 1881; G. Surr, *Min. Eng. World*, **37**, 288, 1912. Potassium can be detected if but 60 parts are present per 1,000,000 parts of solution; if the test be made in the presence of 0·01N-silver nitrate, the sensitiveness of the test is increased to one part per million (L. L. Burgess and O. Kamm, *Journ. Amer. Chem. Soc.*, **34**, 652, 1912). Compare page 416.
[3] Ammoniacal fumes must therefore be absent when the work is in progress.
[4] F. H. van Leent, *Zeit. anal. Chem.*, **40**, 567, 1901; H. Weber, *ib.*, **38**, 171, 1899; W. Autenrieth and R. Bernheim, *Zeit. physiol. Chem.*, **37**, 29, 1902; W. Autenrieth, *Centr. Min.*, 513, 1908; K. Gilbert, *Die Bestimmung des Kaliums nach quantitativer Abscheidung desselben als Kaliumnatriumkobaltinitrit*, Tübingen, 1898; H. R. Christensen and N. Feilberg, *Landw. Versuchs.-Stat.*, **97**, 27, 1921; A. J. Hamburger, *Biochem. Zeit.*, **71**, 415, 1915; **74**, 414, 1916; T. D. Jarrell, *Journ. Assoc. Off. Agric. Chem.*, **1**, 29, 1915; C. V. Garola and V. Braun, *Ann. Falsif.*, **10**, 572, 1917; R. C. Haff and E. H. Schwartz, *Ind. Eng. Chem.*, **9**, 985, 1917; E. Sherrill, *ib.*, **13**, 227, 1921; P. J. van Rysselberge, *ib.*, *Anal. Ed.*, **3**, 3, 1931; W. E. Thrun, *ib.*, *Anal. Ed.*, **5**, 79, 1933; M. E. Pozzi-Escot, *Bull. Soc. chim. Belg.*, **32**, 227, 1923; E. Clerfeyt, *ib.*, **31**, 417, 1922; P. Wenger and C. Héman, *Ann. Chim. anal.*, (2), **2**, 198, 1920; M. Wikul, *Zeit. anorg. Chem.*, **151**, 338, 1926; M. A. Hamid, *Analyst*, **51**, 450, 1926; M. Wikul, *Zeit. anal. Chem.*, **72**, 345, 1927; A. Vassiliev and N. Matveev, *ib.*, **81**, 106, 1930; A. Leulier, L. Velluz and H. Griffon, *Bull. Soc. chim. biol.*, **10**, 891, 1928; A. Thürmer, *Chem. Ztg.*, **52**, 974, 1928; J. H. Dennett, *Malayan Agric. Journ.*, **17**, 341, 1929; C. B. Maw and K. R. Miller, *Proc. Utah Acad. Sci.*, **8**, 61, 1931; E. Remy, *Arch. Pharm.*, **269**, 678, 1931; S. Katakousinos and A. Papadimitriou, *Zeit. Pflanz. Düng.*, **26A**, 166, 1932; E. Rupp and A. Poggendorf, *Apoth. Ztg.*, **47**, 282, 1932; A. H. Lewis and F. B. Marmoy, *Journ. Soc. Chem. Ind.*, **52**, 177T, 1933; *U.S. Geol. Sur. Bull.*, **700**, 214, 1919; K. Scheringa, *Chem. Weekb.*, **30**, 598, 1933; K. L. Malyarov and V. B. Matzkevich, *Zavodskaya Lab.*, **3**, 705, 1934. For the use of silver cobaltinitrite, see R. J. Robinson and G. L. Putnam, *Ind. Eng. Chem. Anal. Ed.*, **8**, 211, 1936; A. M. Ismail and H. F. Harwood, *Analyst*, **62**, 443, 1937.

but the precipitate contains variable quantities of sodium unless the conditions under which the precipitation is made be fairly constant.[1] The precipitate can then be made to approximate closely to dipotassium sodium cobalti-nitrite, $K_2NaCo(NO_2)_6 . H_2O$.[2]

It is maintained by some that the precipitation of potassium as cobalti-nitrite is not advisable because of the variable nature of the precipitate just indicated and because the precipitate is extremely difficult to wash clean. When first formed, the precipitate is granular and settles easily, but it has a tendency to become more or less colloidal as the washing liquids become poor in dissolved salts. The precipitate then filters slowly and is liable to run through the filtering medium. It has been found possible, however, to cope with these difficulties by evaporating the solution containing the precipitate to a pasty mass before filtration and washing. The evaporation also eliminates an error due to the variable character of precipitates formed in solutions of different concentration and variations which occur when the precipitate is allowed to stand in contact with the mother liquid for different lengths of time. Under these conditions fairly satisfactory results have been obtained.

The precipitate need not be ignited and weighed, for it reacts with potassium permanganate as symbolised by the complicated equation :
$$10K_2NaCo(NO_2)_6 . H_2O + 22KMnO_4 + 58H_2SO_4 = 21K_2SO_4 + 5Na_2SO_4 + 10CoSO_4$$
$$+ 22MnSO_4 + 60HNO_3 + 38H_2O.$$
Hence, the precipitate, and accordingly also potassium, can be determined by a volumetric process.[3] It follows from the equation that $22KMnO_4$ are equivalent to $10K_2O$; or 1 c.c. of $0.1N$-$KMnO_4$ $= 0.0008563$ grm. K_2O.

Preparation of the Sample.— One to five grams of the powdered mineral is decomposed by evaporation to dryness with a mixture of sulphuric and

[1] R. H. Adie and T. B. Wood, *Journ. Chem. Soc.*, **77**, 1076, 1900; M. Cunningham and F. M. Perkin, *ib.*, **95**, 1562, 1909; K. A. Hofmann and O. Burger, *Ber.*, **40**, 3298, 1907; E. A. Mitscherlich, K. Celichowski and H. Fischer, *Landw. Vers. Stat.*, **76**, 139, 1912; E. A. Mitscherlich and H. Fischer, *ib.*, **78**, 75, 1912; A. Vürtheim, *Rec. Trav. chim.*, **40**, 593, 1921; L. le Boucher, *Anal. Fis. Quim.*, **23**, 540, 1925; O. M. Kosman, *Journ. Applied Chem.* (*U.S.S.R.*), **6**, 362, 1933; H. W. Lohse, *Ind. Eng. Chem. Anal. Ed.*, **7**, 272, 1935.

[2] S. D. Sunawala and K. R. Krishnaswami (*Journ. Indian Inst. Sci.*, **17A**, 105, 1934; A. Bouat, *Ann. École nat. agr. Montpellier*, **23**, 197, 1935) say that the salt may have 0.5, 1 or 2 molecules of water of crystallisation depending on the conditions of precipitation.

[3] R. H. Adie and T. B. Wood (*l.c.*); W. A. Drushel, *Amer. J. Science*, (4), **24**, 433, 1907; (4), **26**, 329, 555, 1908; *Bull. U.S. Agric. Dept.* (*Chem.*), **152**, 42, 1912; E. L. Baker, *ib.*, **152**, 28, 1912; P. F. Trowbridge, *ib.*, **152**, 184, 1912; L. T. Bowser, *ib.*, **152**, 45, 1912; *Journ. Ind. Eng. Chem.*, **1**, 791, 1909; O. M. Shedd, *ib.*, **1**, 302, 1909; **2**, 379, 1910; R. C. Haff and E. H. Schwartz, *ib.*, **9**, 785, 1917; J. E. Schueler and R. P. Thomas, *ib.*, *Anal. Ed.*, **5**, 163, 1933; E. A. Mitscherlich, K. Celichowski and H. Fischer, *Landw. Vers. Stat.*, **76**, 139, 1912; L. Zaleski, *ib.*, **83**, 221, 1913; H. Fischer, *ib.*, **85**, 139, 1914; W. Selhe, *ib.*, **114**, 321, 1933; F. H. MacDougall, *Journ. Amer. Chem. Soc.*, **34**, 1684, 1912; B. Schmitz, *Mitt. Lebensm. Hyg.*, **4**, 272, 1913; L. L. Burgess and O. Kamm, *Bull. Univ. Illinois*, **10**, 1913; *Chem. Zentr.*, (1), 398, 1915; A. Vityn, *Zhur. Apytn. Agron.*, **13**, 192, 1913; J. L. M. van den Bos, *Chem. Weekb.*, **10**, 182, 1913; L. Galimberti, *Atti II Cong. Naz. Chim. pura appl.*, 1396, 1926; *Chem. Zentr.*, (2), 589, 1928; P. N. Grigoriev and S. S. Korol, *Journ. Chem. Ind.* (*Moscow*), **8**, 68, 1931; W. U. Behrens, *Zeit. Pflanz. Düng. Bodenk.*, **24A**, 289, 1932; I. N. Antipov-Karataev and A. M. Myasnikova, *Proc. Leningrad Dept. Inst. Fert.*, **17**, 69, 1933; L. Jendrassik and J. Szél, *Biochem. Zeit.*, **267**, 124, 1933; Chien Peng, *Science* (*China*), **17**, 542, 1933; P. L. Hibbard and P. R. Stout, *Journ. Assoc. Off. Agric. Chem.*, **16**, 137, 1933; V. I. Tovarnitzki and P. S. Sergeenko, *Zhur. Sakharnoi Prom.*, **2**, 228, 1928; P. S. Sergeenko, *Ukraine Chem. Journ.*, Sci., Pt. 5, 113, 1930; B. Dirks and F. Scheffer, *Das Superphosphat*, **6**, 75, 1930; P. N. Grigor'ev, *Sprechsaal*, **66**, 162, 1933; C. S. Piper, *Journ. Soc. Chem. Ind.*, **53**, 392T, 1934; C. Peng, *Trans. Sci. Soc. China*, **8**, 153, 1934; K. Suzuki and M. Kenjo, *Rep. Govt. Sugar Expt. Sta.*, **2**, 45, 1935; J. Kimura and H. Chiba, *Journ. Sci. Soil Manure, Japan*, **10**, 429, 1936; L. Jendrassik and A. Polgar, *Zeit. anal. Chem.*, **107**, 417, 1937; L. V. Wilcox, *Ind. Eng. Chem. Anal. Ed.*, **9**, 136, 1937.

hydrofluoric acids (page 219). The dry mass is extracted with about 50 c.c. of hot water and boiled with a saturated solution of sodium acetate [1] for 10–15 minutes in a beaker of Jena glass. The precipitated basic acetates of iron, aluminium and titanium are filtered and washed a few times with hot water. The filtrate is boiled with sodium carbonate. The precipitated magnesium and calcium salts are washed with hot water and the filtrate evaporated down to about 15 or 20 c.c.

Precipitation of Potassium Cobaltinitrite.—The solution prepared as just described, or by any other convenient process, is mixed in a porcelain basin with, say, 30 c.c.[2] of Koninck's reagent [3] and 1 c.c. of concentrated acetic acid,[4] evaporated on a water bath down to a pasty consistence [5] and, after cooling, stirred with 25–50 c.c. of water. The liquid is filtered through an asbestos-packed Gooch crucible and the precipitate washed with sufficient water to remove the excess of the reagent.

Volumetric Determination of the Precipitated Cobaltinitrite.—Transfer the precipitate and felt to a 300 c.c. beaker and carefully remove any precipitate adhering to the sides of the crucible by means of a rubber-tipped rod and jet of water. An excess of $0.1N$-$KMnO_4$ is added and the contents of the beaker are boiled until the colour begins to darken. Add 10 c.c. of sulphuric acid (1 : 1),[6] thoroughly stir the mixture and titrate at about 60°–70° with $0.1N$-oxalic acid solution until the pink colour of the permanganate just disappears.[7] The difference between the number of c.c. of the $0.1N$-permanganate added and the number of c.c. of oxalic acid used in the titration, multiplied by 0.0008563 represents the number of grams of K_2O in the given sample. Thus, with 0.5 grm. of a sample of felspar, 50 c.c. of $0.1N$-permanganate were added and 8 c.c. of $0.1N$-oxalic acid were used in the subsequent titration of the

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[1] The solution of 5 grms. of the crystalline salt in water should give no yellow precipitate with sodium cobaltinitrite (Koninck's reagent) after standing 24 hours.

[2] A large excess of Koninck's reagent is needed to ensure the coagulation of the precipitate and prevent its running through the asbestos.

[3] KONINCK'S REAGENT.—Dissolve 30 grms. of cobalt nitrate, $Co(NO_3)_2.6H_2O$, in 60 c.c. of water, add 100 c.c. of a saturated solution (corresponding to about 50 grms.) of sodium nitrite and 10 c.c. of glacial acetic acid. In a few seconds, a brisk effervescence occurs owing to the escape of nitric oxide, the colour of the solution simultaneously changing to a dark yellowish-brown. Since commercial sodium nitrite nearly always contains some potassium salt, some potassium cobaltinitrite usually separates when the mixture has stood. Filter the solution after standing a couple of days. Cobalt nitrate may contain up to 0.3 per cent. of ammonium nitrate—C. S. Piper, *Journ. Soc. Chem. Ind.*, **54**, 157T, 1935. The reagent undergoes very little change in three to four weeks if it is kept in dark-coloured glass bottles. The sensitiveness of the reagent which has been kept some time can be tested by adding a few drops to 5 c.c. of distilled water containing one drop of a 10 per cent. solution of potassium chloride. The reagent can be used if it at once produces a yellow precipitate. The reagent which has decomposed and is accordingly useless for the purpose has lost its yellowish-brown colour and becomes rose-red—W. Autenrieth (*l.c.*). Some prefer to keep the solutions of cobalt nitrate and sodium nitrite in separate bottles and mix the proper proportions for use as required.

[4] The acetic acid prevents subsequent difficulties arising from the sticking of the precipitate to the porcelain dish. If the difficulty still persists, add more acetic acid next time the analysis is made.

[5] If the heat be here too vigorously applied, the viscid liquid is liable to spurt.

[6] F. H. MacDougall (*l.c.*) says: "If the sulphuric acid be added to the yellow salt before the permanganate, the amount of permanganate required will be greater than in the regular method . . . owing to the failure of cobaltic cobalt to oxidise nitrites in sulphuric acid solutions under the conditions of the described method."

[7] If manganese hydroxide sticks to the sides of the beaker, add a slight excess of oxalic acid and loosen the precipitate by means of a rubber-tipped rod. Remove the rod and rinse it, since rubber must not be left in contact with potassium permanganate. Then titrate the excess of oxalic acid with $0.1N$-permanganate.

undecomposed permanganate. Hence, $(50-8) \times 0.0008563 = 0.036$ grm. of K_2O per 0·5 grm. of sample; or the sample contained the equivalent of 7·2 per cent. of potash (K_2O).[1]

Determination of the Potassium in the Cobaltinitrite as Potassium Chloroplatinate or Perchlorate.—According to Autenrieth,[2] the method is most usefully employed as a rapid control process, and for separating the potassium from the other constituents prior to its exact determination as perchlorate or chloroplatinate. In this case, the precipitated cobaltinitrite is collected on a filter-paper and dried; the paper is ashed separately in a platinum crucible and the precipitate added; the whole is then calcined to dull redness for a few minutes and the alkali nitrites extracted with hot water. Filter off the cobalt oxide, evaporate the filtrate to dryness with concentrated hydrochloric acid (sp. gr. 1·124) and determine the potassium as indicated on page 224 or page 231.

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[1] After trying the effect of various salts on the results, Bowser (*l.c.*) said: "The greatest danger seems to exist in the case of $MgCl_2$, the iron and the soluble calcium salts. It is unsafe to trust a determination when any of these metals are present. Adie and Wood advised precipitating out all these interfering metals by boiling with sodium carbonate, and this would seem to be the best procedure." See A. Rauch (*Zeit. anal. Chem.*, 98, 385, 1934) for the determination of the alkalies in the presence of magnesium.

[2] W. Autenrieth, *Centr. Min.*, 513, 1908; A. H. Bennett, *Analyst*, 41, 165, 1916; R. L. Morris, *ib.*, 48, 250, 1923; W. Strecker and A. Jungck, *Zeit. anal. Chem.*, 63, 161, 1923; C. Krügel and A. Retter, *ib.*, 96, 314, 1934; V. Crasu and V. Manole, *Bul. Soc. Chim. Romănia*, 15, 129, 1933. With very small quantities of potassium, M. Delaville and P. Carbier (*Compt. rend.*, 182, 701, 1926) precipitate as cobaltinitrite and determine the cobalt in the precipitate with α-nitroso-β-naphthol (page 420). K. Nowak (*Przemysl Chem.*, 18, 509, 1934) measures the volume of the precipitate in a graduated centrifuge tube.

PART V.

SPECIAL METHODS—ACIDS AND NON-METALS.

CHAPTER XXXVIII.

THE DETERMINATION OF CARBON—FREE AND COMBINED.

§ 299. The Detection of Carbon.

(1) *The Penfield Test.*[1]—An intimate mixture of the substance with precipitated lead chromate is heated in a narrow horizontal hard glass test tube which has a small bulb blown in its underside near the open end. After charging the tube with the mixture, a drop of a saturated solution of barium hydroxide is placed in the bulb. The presence of carbon is shown, on heating, by the formation of a white film of barium carbonate on the surface of the barium hydroxide solution. Carbonaceous impurities in the lead chromate are removed by heating it in the tube in a current of oxygen immediately before use. The test will detect 0·003 mgrm. of carbon.

(2) *Müller's Test.*[2]—A mixture of about 0·02 grm. of the substance with about twenty times its weight of potassium azide, KN_3, is cautiously heated, at first gently and then for two minutes at a red heat. If carbon is present, potassium cyanide is formed, which can be recognised by conversion into Prussian blue. The addition of a little metallic potassium to the reaction mixture renders the test more delicate.

§ 300. The Direct Determination of Carbon.

A rough idea of the amount of carbon in clays and graphites can often be obtained by digesting the clay with sulphuric and hydrofluoric acids. The temperature must not be high enough to cause reaction between the carbon and the sulphuric acid. A slight action can scarcely be avoided. When the acid has done its work dilute the solution with water, filter through a Munroe's crucible or a tared filter-paper, wash[3] and weigh the dried residue. In view of the many theoretical objections which can be urged against this process, it is surprising how good an approximation can be obtained with a little practice.[4]

Graphitic carbon in the presence of other varieties of organic matter (*e.g.* vegetation) which cannot be removed mechanically is determined by Mackintosh[5] by the following process, which is based on Schöffel's method for

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[1] W. G. Mixter and F. L. Haigh, *Journ. Amer. Chem. Soc.*, 39, 374, 1917.

[2] E. Müller, *Journ. prakt. Chem.*, (2), 95, 53, 1917. For the microchemical detection of carbon, see F. Emich, *Zeit. anal. Chem.*, 56, 1, 1917.

[3] Not through asbestos owing to the attack by the acids, unless the acids are neutralised before the filtration.

[4] For filtration with carbon tubes, see fig. 32, page 90; and subsequent combustion of the residue, see page 631. O. Johannsen, *Stahl Eisen*, 30, 456, 1910.

[5] J. B. Mackintosh, *Chem. News*, 51, 147, 1885; R. Schöffel, *Jahrb. geol. Reichsanstalt*, 16, 270, 1866.

purifying graphite:—Melt some potash in a silver crucible. When the fused mass has stopped spitting and is in a state of quiet fusion, add the dry and powdered sample under investigation. Keep the temperature of the mass just above the melting-point of the potash and stir occasionally with a silver wire. Raise the temperature a little towards the end of the fusion. When the decomposition is complete, take up the mass with water, filter through a weighed Gooch crucible, wash with dilute hydrochloric acid and finally with a little ammonia in order to dissolve any silver chloride resulting indirectly from interaction between the potash and the silver crucible. The graphite remains behind, insoluble; it is scarcely attacked by the treatment. Dry and weigh. Mackintosh says the whole operation occupies about two hours.

Löwe[1] fuses the sample with sodium carbonate, digests the resulting cake with water and boils the residue with a solution of sodium hydroxide. The residue is then boiled with hydrochloric acid, washed with water, dried in a weighed filter and its weight determined. Silica, etc., can be determined in the aqueous solution from the fused cake. There is always some doubt in both Löwe's and Mackintosh's processes if the residue is all carbon, and in consequence processes have been devised to burn the carbonaceous residue and estimate the amount of carbon it contains either by "loss on ignition" or as carbon dioxide.

§ 301. The Wet Combustion Process for the Determination of Carbon as Carbon Dioxide.

In the so-called wet combustion process, the finely powdered sample is digested with a mixture of sulphuric acid and chromic acid, or potassium dichromate, or potassium permanganate, or with potassium persulphate alone.[2]

[1] J. Löwe, *Dingler's Journ.*, **137**, 445, 1885; E. Weinschenk, *Zeit. Kryst.*, **28**, 300, 1897.
[2] R. Warington and W. A. Peake, *Journ. Chem. Soc.*, **37**, 617, 1880; C. F. Cross and A. F. Higgin, *ib.*, **41**, 113, 1882; C. F. Cross and E. J. Bevan, *ib.*, **53**, 889, 1888; A. H. Elliott, *ib.*, **22**, 182, 1869; I. K. Phelps, *Zeit. anorg. Chem.*, **12**, 431, 1896; **16**, 85, 1898; R. Finkener, *Mitt. königl. Ver. Anstalt*, Berlin, 156, 1889; *Zeit. anal. Chem.*, **29**, 666, 1890; H. Engel, *ib.*, **85**, 242, 1931; **96**, 319, 1934; R. E. and W. B. Rogers, *Amer. J. Science*, (2), **5**, 352, 1848; (2), **6**, 110, 1848; C. Brunner, *Pogg. Ann.*, **95**, 379, 1855; E. Ullgren, *Liebig's Ann.*, **124**, 59, 1862; P. Fritsch, *ib.*, **294**, 79, 1896; H. Heidenhain, *Techniker*, **14**, 66, 1893; L. Gmelin, *Oester. Zeit. Berg. Hütt.*, **32**, 708, 1884; H. von Jüptner, *ib.*, **31**, 493, 1883; **34**, 67, 83, 1886; F. A. Cairns, *Chem. News*, **25**, 271, 1872; *Amer. Chem.*, **2**, 140, 1872; F. H. Thies, *Chem. Ztg.*, **38**, 115, 1914; P. L. Hibbard, *Journ. Ind. Eng. Chem.*, **11**, 941, 1919; J. E. Adams, *ib.*, *Anal. Ed.*, **6**, 277, 1934; C. B. Pollard and W. T. Forsee, *ib.*, **7**, 77, 1935; A. Franz and H. Lutze, *Ber.*, **57B**, 768, 1924; H. Dieterle, *Arch. Pharm.*, **262**, 35, 1924; M. Nicloux, *Compt. rend.*, **184**, 890, 1927; **189**, 768, 1929; B. Lustig, *Biochem. Zeit.*, **184**, 67, 1927; A. Boivin, *Bull. Soc. chim. biol.*, **11**, 1269, 1929; A. F. Heck, *Soil Sci.*, **28**, 225, 1929; E. Schadendorff and M. K. Zacherl, *Mikrochem.*, **10**, 99, 1931; H. Lieb and H. G. Kraineck, *ib.*, **9**, 367, 1931; N. J. King, *Chem. Eng. Min. Rev.*, **24**, 429, 1932; W. Knop, *Land. Versuchs. Stat.*, **8**, 40, 1866; D. Florentin, *Bull. Soc. chim.*, (4), **35**, 228, 1924; *Chim. Ind.*, **11**, 875, 1924; U. Springer, *Zeit. Pflanz. Düng.*, **11A**, 313, 1928; **12A**, 309, 1928; I. M. Robertson and J. M. Shewan, *Journ. Soc. Chem. Ind.*, **54**, 35T, 1935. Errors—C. F. Cross and E. J. Bevan, *Chem. Ztg.*, **36**, 1226, 1912; F. Ehrenberg, C. Diebel and H. Verkenstedt, *Zeit. anal. Chem.*, **52**, 408, 1913; H. Arnold, *ib.*, **53**, 678, 1914; R. Lorenz, *Zeit. angew. Chem.*, **6**, 313, 395, 411, 635, 1893; L. L. de Koninck, *ib.*, **6**, 536, 1893; A. Ledebur, *Verh. Verein. Beförd. Gewerbfl.*, 8, 280, 1893; C. von Göttig, *ib.*, 8, 321, 1893; W. Hempel, *ib.*, 8, 460, 1893; Report in *Stahl. Eisen*, **14**, 581, 1894; G. Lunge and A. Lwoff, *ib.*, **14**, 624, 1894; Gerstner, *ib.*, **14**, 589, 1894; H. Koch, *Chem. Ztg.*, **18**, 485, 1894; J. A. Wanklyn and W. J. Cooper, *Phil. Mag.*, (5), **7**, 138, 1879; J. Messinger, *Ber.*, **21**, 2910, 1888; **23**, 2756, 1890; E. Ludwig, *Liebig's Ann.*, **162**, 47, 1872; W. L. Morrison, *Foundry*, **43**, 151, 1915; F. K. Cameron and J. F. Breazeale, *Journ. Amer. Chem. Soc.*, **26**, 29, 1904; A. D. Hall, N. H. J. Miller and N. Marmu, *Journ. Chem. Soc.*, **89**, 595, 1906; P. W. Robertson, *ib.*, **109**, 215, 1916; J. W.

The oxygen evolved during the decomposition of the oxidiser converts the carbon to carbon dioxide. The gases are dried and the carbon dioxide is absorbed as indicated below. These methods appear very simple; so they are. But it is not easy to get good results, mainly because of the incomplete combustion of the carbon. It is therefore well to practise the method with a known weight of cane sugar mixed with, say, china clay known to contain no carbon. One gram of cane sugar gives 1·543 grms. of carbon dioxide. In this way confidence in the process may be acquired. Details of the procedure are indicated below. The results are usually a little low.

1. *The Apparatus.*—The clay under investigation is contained in a Corleis' flask,[1] *A* (fig. 122), which is provided with a side and an exit tube, the latter
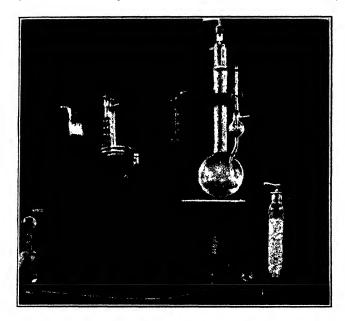
FIG. 122.—Wet Combustion of Carbon.

being connected to the absorption train. The flask is closed by a condenser, *B*, with a ground glass joint. The side tube reaches almost to the bottom of the flask and, in modern forms, is bent to intercept drops from the condenser so that they run quietly into the hot acid in *A*. The upper limb of the side tube terminates in a thistle funnel, *b*, which is closed by a ground glass plug stop-

Ames and E. W. Gaither, *Journ. Ind. Eng. Chem.*, 6, 561, 1914; 7, 561, 1915; C. J. Schollenberger, *ib.*, 8, 1126, 1916; D. D. Waynick, *ib.*, 11, 634, 1919; B. E. Brown, *ib.*, 19, 629, 1927; W. Stepp, *Biochem. Zeit.*, 87, 135, 1918; L. J. Simon, *Compt. rend.*, 174, 1706, 1922; 175, 1070, 1922; 176, 1409, 1923; 177, 122, 265, 1923; L. A. Congdon, F. J. Brown and R. K. Friedel, *Chem. News*, 129, 253, 1924; T. E. Friedemann and A. I. Kendall, *Journ. Biol. Chem.*, 82, 45, 1929; V. Michl, *Časopis Českoslov Lék.*, 12, 57, 1932; *Chem. Zentr.*, (2), 327, 1932; J. W. White and F. J. Holben, *Ind. Eng. Chem.*, 17, 83, 1925; *Journ. Assoc. Off. Agric. Chem.*, 17, 334, 1934; B. E. Dixon, *Analyst*, 59, 739, 1934; L. J. Simon and A. J. A. Guillaumin, *Compt. rend.*, 176, 1065, 1923; E. Wolff, *Anleitung zur chemischen Untersuchung landwirthschaftlich wichtiger Stoffe*, Stuttgart, 1867.

[1] A. Corleis, *Stahl Eisen*, 14, 582, 584, 1894; A. Kleine, *Chem. Ztg.*, 33, 376, 1909. More than a score of different forms of flask have been devised for this purpose. A substitute can readily be improvised from an ordinary flask and condenser. See footnote 2, page 618.

cock, c. The acid for subsequent interaction with the clay is stored in this funnel. A supplementary side limb, below the plug stopcock, is connected with a Fresenius' tower C containing an aqueous solution of caustic potash in the lower part and soda lime in the upper part. The object of the tower C is to remove carbon dioxide from any air subsequently aspirated through the system.[1] The purpose of the condenser is to return steam arising from the flask during an experiment, and so prevent the entry of an excess of moisture into the absorption tubes. The gases travelling past the condenser traverse a White's [2] absorption tube D containing an acid solution of silver sulphate [3] to absorb chlorine and vapours of sulphur compounds. The gases then pass through a capillary tube E of silica [4] or platinum, heated to a dull redness by means of the Bunsen burner F. The object of this tube is to oxidise any hydrocarbons or carbon monoxide which may have escaped complete oxidation by the chromic acid in the Corleis' flask.[5] The gases are then dried by passing through a Müller's absorption tube G. This tube contains concentrated sulphuric acid. The tube G must follow the hot capillary tube E, since sulphuric acid is liable to absorb gaseous hydrocarbons. Any carbon dioxide in the gas is then absorbed by the weighed potash bulb [6] H, which has a calcium chloride tube I attached. A Drechsel's wash-bottle,[7] containing

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[1] For the difficulties involved in removing the last traces of carbon dioxide from air, see C. W. Eliot and F. H. Storer, *Proc. Amer. Acad.*, 5, 62, 1861; *Chem. News*, 3, 178, 1861; R. E. and W. B. Rogers, *l.c.*; C. Brunner, *Pogg. Ann.*, 24, 571, 1832; H. Hlasiwetz, *Wiener Akad. Ber.*, 20, 189, 1856; R. Fresenius, *Zeit. anal. Chem.*, 4, 177, 1865; A. Friedrich, *Zeit. angew. Chem.*, 36, 481, 1923.

[2] J. T. White, *Chem. News*, 58, 166, 1888. Mitscherlich's tube (A. Mitscherlich, *Zeit. anal. Chem.*, 15, 389, 1876) or various other forms of absorption tube may be used and also other types of flask. Thus, a distillation flask with a three-hole rubber stopper fitted with a tap funnel, a reflux condenser and a gas leading tube dipping to the bottom of the flask, and connected, when required, with a suitable absorption apparatus for removing carbon dioxide. L. L. de Koninck (*Zeit. anal. Chem.*, 27, 463, 1888) suggests adding the silver sulphate to the contents of the flask A; but although diluted sulphuric acid (2 acid, 1 water) does not appear to act on silver chloride (J. Volhard, *ib.*, 18, 281, 1879), concentrated sulphuric acid decomposes silver chloride with the evolution of hydrogen chloride (A. Sauer, *ib.*, 12, 176, 1873; L. Blum, *ib.*, 28, 450, 1889). Hence de Koninck's proposal will not work; nevertheless the addition of silver chromate is often advocated. A. Wolkowicz (*Zeit. angew. Chem.*, 7, 165, 1894) recommends the addition of an excess of a 20 per cent. solution of copper sulphate to prevent the evolution of hydrogen sulphide from soluble sulphides.

[3] SILVER SULPHATE SOLUTION.—Dissolve 0·624 grm. of silver sulphate in water, add 5 c.c. of normal sulphuric acid and make the solution up to 100 c.c. The solution is $\frac{1}{25}E$. A tube containing warm lead dioxide is sometimes used to absorb sulphurous gases and halogens. If the lead dioxide be free from lead monoxide, as is the case with "Dennstedt's lead dioxide," there is no danger of the absorption of carbon dioxide. M. Dennstedt and F. Hassler, *Zeit. anal. Chem.*, 42, 417, 1903; M. Dennstedt, *ib.*, 41, 525, 1902; F. Kopfer, *ib.*, 17, 28, 1878; C. M. Warren, *Amer. J. Science*, (2), 41, 40, 1866. Sometimes a heated tube containing silver gauze or wire is used—F. Kopfer, *Zeit. anal. Chem.*, 17, 28, 1878. The silver is restored by heating in a current of hydrogen—K. Kraut, *ib.*, 2, 242, 1863. Antimony is sometimes recommended for removing chlorine. A copper spiral was used by C. Glaser, *Liebig's Ann. Suppl.*, 7, 213, 1870; G. Städler, *Liebig's Ann.*, 69, 334, 1849. For fluorine, see H. Moissan, *Compt. rend.*, 107, 992, 1888; A. Völcker, *Chem. Gaz.*, 7, 245, 1849.

[4] M. Widemann, *Chem. Ztg.*, 33, 1186, 1909.

[5] C. F. Mabery, *Journ. Amer. Chem. Soc.*, 20, 510, 1898; G. Auchy, *ib.*, 20, 243, 1898; J. Widmar, *Zeit. anal. Chem.*, 29, 160, 1890; *Chem. News*, 62, 274, 1890; J. W. Langley, *ib.*, 62, 218, 1890; *Trans. Amer. Inst. Min. Eng.*, 19, 614, 1890; A. von Reis, *Stahl Eisen*, 14, 581, 1894; J. J. Messinger, *Ber.*, 21, 2910, 1888; A. Müller, *Chem. Ztg.*, 28, 795, 1904.
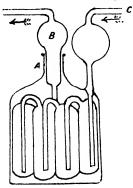
[6] We prefer Berl's or Landsiedl's form of potash bulb for the reasons indicated on page 622. N. J. King (*Chem. Eng. Min. Rev.*, 24, 429, 1932) prefers a solid absorbent, such as "ascarite," for the carbon dioxide, rather than aqueous solutions; "sofnolite" is also frequently used. See also footnote 2, page 619. The carbon dioxide can also be absorbed in a standard solution of potash or baryta, with subsequent back-titration.
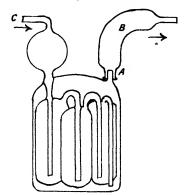
[7] E. Drechsel, *Zeit. anal. Chem.*, 15, 446, 1876.

potash, protects the weighed potash bulb from atmospheric carbon dioxide. The open end of the train J is connected later on with an aspirator or suction apparatus in order that a current of air may be drawn through the system when required. The whole may be mounted on a wooden stand or on a Müller's retort stand as shown in the diagram. The condenser is connected with the tubes in the upper part of the stand by means of rubber tubing. The lower tubes of the stand are respectively connected with the water supply and the sink.

2. *Charging the Absorption Bulbs.*—The Berl's or Landsiedl's potash bulb (figs. 123 and 124) is kept in a desiccator over sulphuric acid or calcium

Fig. 123.—Berl's Potash Bulbs.   Fig. 124.—Landsiedl's Potash Bulbs.

chloride and it should stand in the balance case about an hour before each weighing. This apparatus is filled with an aqueous solution of caustic potash.[1] Place the potash solution in an evaporating basin; remove the guard tube B; attach a piece of rubber tubing, or a suction tube, to the end which was attached to the guard tube; dip the opposite end in the potash solution and suck at the rubber tube until the bulbs are nearly three-fourths full. Do not suck too vigorously or potash may be drawn into the mouth. Clean that part of the apparatus C which dipped in the solution by means of filter-paper. Now fill the guard tube B by placing a plug of glass-wool at the end of the tube; then a layer of fragments of granular (not fused) calcium chloride, less than half a centimetre in diameter and sifted free from dust; then a similar layer of fragments of soda lime;[2] and finally another plug of glass-wool.[3] The joint A

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[1] POTASSIUM HYDROXIDE SOLUTION.—A solution of specific gravity 1·4 is made by dissolving 2 parts of the solid in 3 parts of water by weight. Caustic potash is better than caustic soda, since sodium bicarbonate is less soluble than the corresponding potassium salt. The latter is therefore less likely to block the tubes by crystallising out. If the potash should contain any nitrites high results may be obtained, owing to the formation of nitrates —S. C. Jutsum, *Chem. News*, **41**, 17, 1880. For the relative efficiency of the different absorption media, see R. Fresenius, *Zeit. anal. Chem.*, **5**, 87, 1866; J. Löwe, *ib.*, **9**, 220, 1870.

[2] Soda lime loses moisture in air dried by calcium chloride or concentrated sulphuric acid. Hence some prefer bits of potash in place of the soda lime, but I. Guareschi (*Supp. Ann. all'Enciclopedia di Chimica*, 1915) shows that soda lime, prepared from calcium oxide and a solution of sodium hydroxide, is a better absorbent than solid potash for carbon dioxide. Soda lime is also a good absorbent for chlorine, bromine, hydrogen chloride, hydrogen bromide, nitrogen peroxide and carbonyl dichloride. Much heat is evolved when hydrogen sulphide is absorbed.

[3] If the soda lime tubes be packed too tightly, the expansion which occurs as the solid becomes moist may burst the tubes. It is best to interpose layers of glass-wool between the fragments of soda lime. Calcium chloride may contain basic chlorides or free lime, which

is slightly greased. The potash apparatus will absorb about 0·2 grm. of carbon dioxide without re-filling. The contents of the potash apparatus are protected, when not in use, by glass caps ground on the free ends, or by short pieces of rubber tubing—2 cm. long—with one end closed by a plug of glass rod about 1·5 cm. long, and rounded at both ends. Before a weighing is made the apparatus is wiped with a clean, lint-free cloth and the caps are removed; after weighing they are immediately replaced. The total weight of a charged Landsiedl's potash bulb is about 60 grms.

The lower part of the Fresenius' tower C is filled to a depth of about 2 cm. with potash lye (sp. gr. 1·4). A plug of glass-wool is placed in the constricted part and fragments of dust-free soda lime, rather coarser than those used for the tube B, are placed in the upper part. When not in use, the ends of the absorption tubes should be plugged with rubber tubing and glass rods to shut off the air. The stoppers of C and G render plugs unnecessary.

3. *Charging the Combustion Flask.*—Transfer, say, 1 grm. of the clay,[1] finely powdered and dry (110°), to the Corleis' flask and add from 5–10 grms. of coarsely granular dry potassium dichromate.[2] If the clay be rich in organic matter less clay may be taken and the clay is often advantageously mixed with about 10 grms. of dry calcined sand—say Calais sand. Add about 10 c.c. of water[3] and shake up the mixture, taking care that none of the powder is left stranded above the level of the liquid in the flask. Connect the apparatus as shown in the diagram (fig. 122), and aspirate air throughout the flask and train of absorption tubes for about 10 minutes. Weigh the potash apparatus and place it in the position shown in fig. 122.

4. *The Oxidation.*—Close the stopcock c, light the Bunsen burner F. Pour concentrated sulphuric acid[4] into the bulb b and allow the acid to run very slowly into the flask. If no vigorous action occurs, raise the temperature of the flask very slowly.[5] The bubbles of gas should not at any time pass so rapidly that they cannot be easily counted. If the velocity of the reaction be too rapid, the gases may pass through the potash bulbs without being washed free from carbon dioxide and the calcium chloride tube may not absorb the moisture driven from the potash bulbs. The bulb b should be emptied before the flask is warmed, so that the stopcock can be quickly opened in case a sudden pressure be generated in the flask. If the flask should burst and hot concentrated sulphuric acid be sprayed about the operator, the conse-

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absorb carbon dioxide and lead to incorrect results if such be placed in tubes *before* the potash apparatus. The faulty calcium chloride will react alkaline to litmus. To render the contamination inert, it is usual to pass a stream of dry carbon dioxide through the calcium chloride for a couple of hours, and remove the carbon dioxide by passing a current of dry air over the calcium chloride for half an hour. C. Winkler (*Zeit. anal. Chem.*, 21, 545, 1882) denies the efficacy of the treatment. He maintains that the lime in the chlorides cannot be completely saturated with carbon dioxide, since the inside of the granules remains caustic after the treatment. In any circumstances the error mentioned by Winkler is very small, and in the present case this difficulty does not enter into the problem.

[1] The amount of clay to be taken depends on the amount of carbon it contains. The present sample was a black Devonshire ball clay.

[2] Since potassium dichromate is difficult to obtain free from carbon dioxide, W. Stepp (*Biochem. Zeit.*, 87, 135, 1918) prefers to use chromic acid.

[3] Low results are obtained unless the relative amount of water is small—J. W. Ames and E. W. Gaither, *Journ. Ind. Eng. Chem.*, 6, 561, 1914; T. E. Friedemann and A. I. Kendall, *Journ. Biol. Chem.*, 82, 45, 1929.

[4] W. Stepp (*l.c.*) frees the sulphuric acid from carbonaceous impurities by first heating it with dichromate and then with permanganate. About 50 c.c. of sulphuric acid (sp. gr. 1·84) are needed.

[5] The dichromate may be dissolved in the sulphuric acid before it is mixed with the clay, as recommended by F. K. Cameron and J. F. Breazeale (*Journ. Amer. Chem. Soc.*, 26, 29, 1904).

quences would be serious ! With a Corleis' flask, the condenser tube or the plug stopcock will be lifted if the pressure becomes very great.[1] A wire gauze between the gas and the Corleis' flask is preferable to a sand bath or to an asbestos or silica plate, because the temperature of the flask is then under better control. When all the carbon is oxidised, a current of air is aspirated through the system for about 10 minutes.

5. *The Weighings.*—1 grm. of clay was treated as just described and the readings obtained were as follows:—

Weight of potash bulbs (after)	78·7221 grms.
Weight of potash bulbs (before)	78·5637 grms.
Carbon dioxide absorbed	0·1584 grm.

Every 44 grms. of carbon dioxide are equivalent to 12 grms. of carbon; hence, 0·1584 grm. of carbon dioxide is equivalent to 0·0432 grm. of carbon per 1 grm. of clay; or the sample has 4·32 per cent. of carbon. It will be observed that an experimental error of 1 per cent. only makes about 0·3 per cent. difference in the determination of the carbon.[2] *The agreement in a number of duplicates does not prove that the results are accurate.* As indicated on page 151, such an agreement shows nothing more than that the method of analysis used will give consistent results when conducted in a uniform way. Suppose a constant percentage of carbon escaped decomposition, the duplicates would be consistently too low. In order to make reasonably sure that a result is accurate it is necessary to show that a similar result is obtained by several different methods. The time involved is out of question in commercial work; but it is necessary in establishing the accuracy of a method of measurement when it is not possible to operate with mixtures of known composition.[3]

As stated above, there is no special reason why the particular form of apparatus here recommended should be adopted. Once the principle is mastered, there will be no difficulty in devising innumerable modifications. Fresenius, for instance, used only U-tubes and flasks connected by rubber and glass tubing, but he needed nine U-tubes and two flasks! By means of more efficient absorbing apparatus, it is now possible to make the apparatus more compact and to lessen the labour of fitting up the apparatus. The time-factor here again presses upon us. A neat and compact apparatus frequently costs more than a home-made apparatus, but in routine work the neat and compact apparatus frequently saves time and renders it less easy to make mistakes.

§ 302. The Errors in Analyses involving the Weighing of Absorption Tubes.

It requires some practice to get constant results. In addition to the precautions already mentioned, it may be useful to point out a few more sources of danger.[4]

1. The air leaving the weighed potash bulbs should have the same state of humidity as the air which enters; otherwise, a loss or gain of moisture might

[1] An explosion might occur if boiling sulphuric acid struck the condenser and caused it to crack. At any rate, a stream of cold water from the cracked condenser descending into the boiling sulphuric acid would make things unpleasant ! Hence the acid should boil without bumping.

[2] For conversion table CO_2 to C, see H. Loomis, *Journ. Ind. Eng. Chem.*, 8, 637, 1916.

[3] See the cane sugar and china clay experiment, page 617. Dittrich's experiments, page 243. B. Blount and A. G. Levy, *Analyst*, 34, 94, 1909; A. G. Levy, *ib.*, 37, 392, 1912; H. Islam, *Journ. Ind. Eng. Chem.*, 3, 577, 1911; H. Brearley, *Chem. News*, 84, 23, 1901.

[4] G. Auchy, *Journ. Amer. Chem. Soc.*, 20, 528, 1898; H. Heidenhain, *ib.*, 18, 1, 1896.

ensue. A second weighed absorption tube containing, say, concentrated sulphuric acid can be placed after the potash bulb to prove that no moisture escaped absorption in the absorption tubes during an experiment. A *témoin* (witness) tube in the form of a duplicate potash bulb may follow the one used for the absorption. The object of this vessel is to make sure that all the carbon dioxide passing through the system is absorbed in the first potash bulbs. If the gas from the clay has a tendency to come off in sudden rushes, this second bulb is a necessary adjunct to the train (fig. 122).

2. The volume of the weighed bulbs is often great enough to render necessary the corrections mentioned on page 15 for differences in the buoyancy of air due to variations of temperature and pressure during an experiment.

3. There is a difficulty in weighing the potash apparatus on account of the difference in the amounts of moisture and gases condensed on the surface of the glass before and after a combustion. This is particularly noticeable in damp atmospheres, when the effect may be great enough to vitiate an analysis. The glass is exposed to variations in humidity due to the proximity of the absorption apparatus to the sources of heat; to heat generated by the absorption of carbon dioxide by the potash; to handling with moist or greasy fingers. The apparatus is usually wiped [1] with a clean, soft linen or silk cloth so that the glass does not come in contact with the fingers and then allowed to stand in the balance case half an hour before weighing. If the apparatus on re-wiping has the same weight as before, the result is supposed to be right. The simpler types of potash apparatus with a small surface lend themselves more readily to this treatment than the Geissler's and Liebig's potash bulbs once regularly used in organic analysis. These tubes are too complex to permit a thorough wiping. Regnault and Stas used a tare in the form of an empty potash bulb of similar shape and volume to the one in use, and placed on the "weights" side of the balance during the weighings.[2] These remarks also apply to the determination of moisture by absorption in weighed U-tubes.

Although many different forms of absorption tube are available, our choice is thus limited by the above considerations. Hence, absorption bulbs of the type of Schiff's, Arnold's, Gomberg's, Landsiedl's, Carrasco's, Anderson's, Delisle's, Wetzel's, Classen's, Berl's, Bender and Hobein's, are preferred to the time-honoured bulbs of Liebig, Mitscherlich, Koninck, Schloesing and Geissler.[3] Berl's (fig. 123) and Landsiedl's (fig. 124) bulbs are used in this work. There is a disadvantage in not having the liquid in the different bulbs in communication, because when one bulb is saturated the liquid cannot diffuse into the others. One bulb is thus thrown out of action.[4] For similar reasons to those just con-

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[1] Note the possible electrification of glass vessels on rubbing, and its influence on weighing, mentioned on page 4. This error may run as high as 0·020 grm. (E. Bornemann, *Chem. Ztg.*, 32, 125, 220, 1908). The charge disappears slowly by repeatedly touching the apparatus with the fingers. The electrification is more likely to occur in dry, frosty weather.

[2] The magnitude of the error is reduced by the use of this counterpoise.

[3] W. C. Anderson, *Journ. Soc. Chem. Ind.*, 18, 119, 1899; A. Delisle, *Dingler's Journ.*, 279, 167, 1891; A. Dettloff, *Zeit. anal. Chem.*, 46, 717, 1907; C. Mann, *ib.*, 32, 186, 1893; S. Schiff, *ib.*, 28, 679, 1889; A. Landsiedl, *Oester. Chem. Ztg.*, 5, 31, 1903; M. Gomberg, *Journ. Amer. Chem. Soc.*, 18, 941, 1896; C. M. Johnson, *ib.*, 28, 862, 1906; O. Carrasco, *Chem. Ztg.*, 31, 342, 1907; E. Berl, *ib.*, 34, 428, 1910; G. Schöler, *ib.*, 29, 569, 1905; L. Dufty, *Chem. News*, 87, 289, 1903; A. E. Hill, *ib.*, 98, 38, 1908; H. L. Fisher, *Journ. Ind. Eng. Chem.*, 8, 368, 1916; S. F. Acree, *Amer. Chem. Journ.*, 35, 309, 1906; J. Wetzel, *Ber.*, 33, 3393, 1900; 36, 161, 1903; A. Friedrich (*Zeit. angew. Chem.*, 36, 481, 1923) says that new absorption bulbs should be steamed out before using for the first time.

[4] J. Löwe, *Zeit. anal. Chem.*, 7, 224, 1868.

sidered, we recommend, later on, a calcium chloride tube with but a small surface exposed to the atmosphere.

When the carbon dioxide is determined by passing the gas through aqueous barium hydroxide, filtering off and weighing the barium carbonate, or by titrating the residual barium hydroxide,[1] the error is eliminated. This is also the case when the volume of the gaseous carbon dioxide is determined.[2]

§ 303. The Detection of Carbon Dioxide.

The presence of carbonates is indicated by a sudden effervescence when the substance is treated with dilute acids—sulphuric, hydrochloric or phosphoric acid. An excess of acid should be used, since some bicarbonates are soluble in water. The experiment is made by placing a little of the substance in a test tube, covering it with dilute hydrochloric acid, and warming the contents of the tube. The carbon dioxide which is formed is heavier than air and may be poured into a second test tube containing a little lime or baryta water.[3] If the second test tube be shaken, a turbidity will be produced if carbonates be present in the sample under investigation.[4] A drop of lime water hanging from the end of a glass rod held just inside the test tube which contains the substance under investigation will show a film of calcium carbonate if carbonates be present.

The test may also be conducted in the following way.[5] Draw out the end of a narrow test tube as shown at A, fig. 125, and fit a capillary funnel or conical tube as shown at B. Put the substance under investigation in the tube A, and a drop of baryta

FIG. 125.

[1] U. Kreusler, *Zeit. Chem.*, (2), 2, 292, 1866; *Zeit. anal. Chem.*, 5, 216, 1866; P. Claesson, *Ber.*, 9, 174, 1876; M. Pettenkofer, *Journ. Chem. Soc.*, 10, 292, 1857; *Journ. prakt. Chem.*, (1), 82, 32, 1861; (1), 85, 179, 1862; *Liebig's Ann. Suppl.*, 2, 23, 1863; W. Spring and L. Roland, *Mém. Acad. Roy. Belg.*, 37, 1, 1887; J. A. Aupperle, *Journ. Amer. Chem. Soc.*, 28, 858, 1906; A. Grégoire, J. Hendrick, E. Carpiaux, and E. Germain, *Ann. Chim. anal.*, 18, 1, 1913; A. Dorner, *Zeit. physiol. Chem.*, 88, 425, 1913; A. Warburg, *ib.*, 61, 261, 1909; A. Gronzea, *Bul. Soc. Stiinte Bucuresti*, 16, 156, 1914; E. Truog, *Journ. Ind. Eng. Chem.*, 7, 1045, 1915; P. L. Hibbard, *ib.*, 11, 941, 1919; N. J. King, *Chem. Eng. Min. Rev.*, 24, 429, 1932; M. Nicloux, *Compt. rend.*, 184, 890, 1927; Anon., *Chem. Ztg.*, 46, 706, 1922.

[2] J. Wiborg, *Berg. Hütt. Ztg.*, 46, 233, 1887; A. A. Blair, *Journ. Amer. Chem. Soc.*, 18, 223, 1896; G. Lunge and L. P. Marchlewski, *Zeit. angew. Chem.*, 4, 229, 412, 1891; E. Donath and W. Ehrenhofer, *Oester. Zeit. Berg. Hütt.*, 45, 285, 1897; W. Hempel, *Verh. Verein. Beförd. Gewerbfl.*, 8, 640, 1893; J. R. Cain, *Journ. Ind. Eng. Chem.*, 8, 368, 1916; C. J. Schollenberger, *ib.*, 8, 417, 1916.

[3] The lime water should be kept in contact with calcium carbonate so that the solution is saturated with calcium carbonate, otherwise minute amounts might escape detection owing to the slight solubility of calcium carbonate in lime water—C. L. Berthollet, *Ann. Chim.*, 3, 68, 1789; H. A. von Vogel, *Schweigger's Journ.*, 33, 207, 1821; F. H. Storer, *Amer. J. Science*, (2), 25, 42, 1858; H. N. McCoy and S. Tashiro, *Intern. Cong. App. Chem.*, 8, i, 361, 1913; J. F. Barker, *Journ. Ind. Eng. Chem.*, 9, 787, 1917.

[4] Owing to the fact that air contains carbon dioxide, baryta water will nearly always give a turbidity with a blank test. Hence, the turbidity produced by the carbonate should be more intense than the turbidity produced by the blank test. The two should show a marked difference. J. Petersen (*Zeit. anorg. Chem.*, 88, 234, 1914) detects carbonates in the presence of sulphides by decomposition with hydrochloric acid in the presence of zinc. The hydrogen, generated from the latter, carries the gases into an absorption flask, charged with 3 per cent. hydrogen peroxide solution to remove the hydrogen sulphide and then into a second flask containing lime water

[5] O. Rössler, *Ber.*, 20, 2629, 1887; O. F. Stafford, *Journ. Amer. Chem. Soc.*, 40, 622, 1918. In special cases, the test must be conducted in air free from carbon dioxide—see F. P. Treadwell, *Analytical Chemistry*, New York, 1, 307, 1903. Consult any work on qualitative analysis for confirmatory tests.

water in *B*. Dip the test tube at *A* in hydrochloric acid.[1] The presence of carbonates is shown by a white cloud forming in the baryta water as carbon dioxide passes through.

§ 304. The Rapid Determination of Carbon Dioxide in Carbonates.

Fresenius remarks that there are few methods of analysis equal in accuracy to a process somewhat similar to that described on page 616; but it requires care and time, and other investigators[2] have come to the conclusion that the wet process is not so satisfactory as dry combustion. There are several short cuts, some of which are quite satisfactory; others, not so accurate, are only justified when time must be saved. There is a remarkable variety[3] of remarkably ingenious and compact instruments in which the acid, the carbonate and the desiccating agent are placed in separate compartments of one instrument. All are weighed together. The acid is then brought in contact with the carbonate and, when the action is over, the loss in weight represents the carbon dioxide which has left the system. It is not easy to get a degree of accuracy greater than to about half per cent. with these instruments, except by taking precautions involving the expenditure of nearly as much time as the gravimetric process next described. If an accuracy of about one per cent. be desired,[4] we can select an apparatus from the dealers' catalogues, rejecting those which are cumbrous, fragile, difficult to clean and expensive. Rohrbeck's and Schrötter's are favourite forms.[5]

FIG. 126.—
Schrötter Apparatus.

The standard form of Schrötter apparatus is shown in fig. 126. It is charged for use by pouring concentrated sulphuric acid into the gas washing bulb *A* until the port *a* is submerged to a depth of 5 to 10 mm. The

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[1] Dilute sulphuric acid does not always produce effervescence with magnesite, siderite and dolomite. The "best acid" to use depends upon the nature of the carbonate. Sulphuric acid is suitable for alkali carbonates; hydrochloric acid for magnesium and calcium carbonates; and nitric acid for lead carbonates—white lead. With nitric and hydrochloric acids there is always a danger of losing a little acid, since some acid may be carried out of the system with the carbon dioxide, especially if the latter comes off rapidly. A. Mayer (*Landw. Vers. Stat.*, **51**, 339, 1899) says that if ferrous carbonate be present, dilute acetic acid is best (1 acid, 2 water), since ferrous carbonate is not then attacked, while magnesium and calcium carbonates are attacked. H. Bornträger (*Zeit. anal. Chem.*, **29**, 141, 1890) prefers nitric to hydrochloric acid for small quantities, because hydrogen chloride and chlorine gases are not absorbed by the drying agent—sulphuric acid—whereas nitric and nitrous gases are.

[2] F. Ehrenberg, C. Diebel and H. Verkenstedt, *Zeit. anal. Chem.*, **52**, 408, 1913; L. A. Congdon, F. J. Brown and R. K. Friedel, *Chem. News*, **129**, 253, 1924. See also footnote 2, page 616, under "Errors."

[3] See the dealers' catalogues for a few of the multitudinous forms which have been invented. For a process based on the fusion of sample with sodium paratungstate, see F. A. Gooch and S. B. Kuzirian, *Amer. J. Science*, (4), **31**, 497, 1911. The loss in weight of the mixture after fusion represents the carbon dioxide expelled. Processes like this have a limited application. See page 585.

[4] The results are better with substances rich in carbonates.

[5] A. R. von Schrötter's (*Ber. Wien. Acad.*, **63**, 471, 1871), J. Davies' (*Brit. Pat. No.* 533209, 1908), J. L. Kreider's (*Amer. J. Science*, (4), **19**, 188, 1905; *Zeit. anorg. Chem.*, **44**, 154, 1905; *Chem. News*, **93**, 62, 1906), C. H. Cribb's (*Analyst*, **21**, 62, 1896), are useful forms.

acid (about 5–10 c.c.) for reaction with the carbonate [1] is placed in bulb B and the ground glass joint b, b between the upper and lower halves of the apparatus is well lubricated. After standing in the balance case for a short time, the apparatus is weighed. About a gram [2] of the carbonate is placed in the receptacle C, care being taken that none of the lubricant is lost when the two halves are detached. The apparatus is again weighed. Remove stopper c and allow the acid in B to enter C *via* the tap d at such a rate that the evolved gas escapes sufficiently slowly to be dried on passage through the sulphuric acid in A. When the reaction is over, a slow current of air [3] is aspirated through the system for 5–10 minutes by applying suction at e and connecting B to a soda lime and calcium chloride tube. The lower portion of C is meanwhile immersed in water at a temperature of 80°–90°. The apparatus is then allowed to cool down to room temperature with tap d open. When cool, stopper c is replaced and the apparatus once more weighed. The loss in weight represents the carbon dioxide which has left the system.[4]

The following numbers represent the results which may be expected:

Used ($CaCO_3$) .	0·2153	0·2011	0·2004	0·2006	0·2020	0·2018 grm.
Found ($CaCO_3$)	0·2149	0·2010	0·1999	0·2003	0·2017	0·2017 grm.
Error . .	−0·0004	−0·0001	−0·0005	−0·0003	−0·0003	−0·0001 grm.

§ 305. The Gravimetric Determination of Carbon Dioxide.

With clays containing carbonates it may be necessary to determine the carbon dioxide independently of the carbon. Hence the carbon dioxide from the decomposition of the carbonate is subtracted from the total carbon dioxide obtained on combustion. The difference gives the carbon dioxide derived from the combustion of the carbonaceous matter in the clay. The carbon dioxide can be accurately determined in an apparatus (fig. 122) modified as indicated in fig. 127.[5] The silica capillary is replaced by a double U-tube E, the first half of which is filled with pumice saturated with anhydrous copper sulphate,[6] and the other half with calcium chloride. The White's tube D

[1] See footnote 1, page 624. For the use of perchloric acid for decomposing carbonates, see C. A. Jacobson and J. W. Haught, *Ind. Eng. Chem. Anal. Ed.*, **2**, 334, 1930; *Bull. West Va. Univ. Sci. Assoc.*, **2**, No. 4, 8, 1930; C. Mahr, *Zeit. anal. Chem.*, **97**, 93, 1934.

[2] The amount is determined by the percentage of carbonates in the given sample. We generally have a rough idea. Two or three grams may be used when the substance is poor in carbonates.

[3] If the material contains ferrous oxide, this may become oxidised when the carbon dioxide is replaced by air. If complete oxidation of the ferrous iron occurs, the reported percentage of carbon dioxide will be 0·11 per cent. too low for every 1 per cent. of FeO present. In such cases it is recommended that the carbon dioxide should be replaced by nitrogen instead of air.

[4] See L. A. Sayce and A. Crawford, *Journ. Soc. Chem. Ind.*, **41**, 57T, 1922, for a review of methods of the above type.

[5] R. Fresenius, *Quantitative Chemical Analysis*, London, **2**, 340, 1876; *Zeit. anal. Chem.*, **14**, 174, 1875; A. Classen, *ib.*, **15**, 288, 1876; L. H. Borgström, *ib.*, **53**, 685, 1914; H. Kolbe, *Liebig's Ann.*, **119**, 130, 1861; J. Hessert, *ib.*, **176**, 136, 1875; J. Volhard, *ib.*, **176**, 142, 1875; H. Rose, *Pogg. Ann.*, **116**, 131, 1862; J. Persoz, *Compt. rend.*, **53**, 239, 1861; L. T. Bowser, *Journ. Ind. Eng. Chem.*, **4**, 203, 1912; H. W. Brubaker, *ib.*, **4**, 599, 1912; E. W. Gaither, *ib.*, **4**, 611, 1912; W. H. MacIntyre and L. G. Willis, *ib.*, **7**, 227, 1915; E. Truog, *ib.*, **7**, 1045, 1915; W. H. Waggaman, *ib.*, **8**, 41, 1916; H. B. Hutchinson and K. Maclennan, *Journ. Agric. Science*, **6**, 323, 1914; A. Suchier, *Zeit. angew. Chem.*, **27**, 527, 1914; F. K. Cameron and J. F. Breazeale, *Journ. Amer. Chem. Soc.*, **26**, 29, 1904; H. V. Thompson in G. Lunge and C. A. Keane, *Technical Methods of Chemical Analysis*, London, **3**, 1, 1931; B. E. Dixon, *Analyst*, **59**, 739, 1934.

[6] F. Stolba, *Dingler's Journ.*, **164**, 128, 1862; *Zeit. anal. Chem.*, **10**, 76, 1871; R. Fresenius, *ib.*, **14**, 174, 1875. The pumice is prepared by sifting about 60 grms. of fragments of pumice, about the size of peas, free from dust. The fragments are placed in an evaporating basin with

contains sulphuric acid.   The other tubes are filled as indicated in the wet combustion process for carbon.

The amount of clay to be taken for an experiment depends upon the amount of carbonates present.   From 5 to 50 grms. of the dried clay are
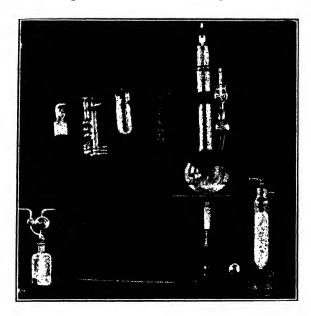
Fig. 127.—Determination of Carbon Dioxide in Carbonates.

transferred to the flask and made into slip with boiled distilled water, free from carbon dioxide.   Hydrochloric or sulphuric acid is added slowly by opening the plug cock.[1]   When effervescence [2] has ceased and enough acid has been added to decompose all the carbonates, the flask is gently heated for about 15 minutes while a current of air is slowly aspirated through the system.

In illustration of the weighings, the following numbers may be cited. 2 grms. of clay were treated with dilute hydrochloric acid and:

Weight of potash bulbs (after)	78·1863 grms.
Weight of potash bulbs (before)	78·1326 grms.
Carbon dioxide	0·0537 grm.

0·0537 grm. of carbon dioxide per 2 grms. of clay represents 2·68 per cent. of carbon dioxide, or 6·11 per cent. of calcium carbonate, since weight of carbon dioxide multiplied by 2·27454 represents the corresponding amount of calcium carbonate, $CaCO_3$; and if the weight of carbon dioxide be multiplied by 1·2745 the corresponding amount of calcium oxide, CaO.   The carbon dioxide may be wholly or in part combined as magnesium carbonate; as dolomite; as

a concentrated solution of copper sulphate (30–35 grms.).   Evaporate the solution to dryness with constant stirring.   Heat 4 or 5 hours in an air bath at 150°–160°, not more, or sulphur dioxide will be formed.   The pumice so prepared will remove hydrogen sulphide and hydrogen chloride from the gases.

[1] For perchloric acid, see footnote 1, page 625.

[2] If the substance froths and foams, it may be necessary to use a comparatively large flask.

ferrous carbonate (siderite); or a basic iron carbonate. If w denotes the weight of carbon dioxide, we have

$2\cdot2745w = $ Per cent. calcium carbonate, $CaCO_3$
$1\cdot9164w = $ Per cent. magnesium carbonate, $MgCO_3$
$2\cdot0954w = $ Per cent. dolomite, $MgCO_3.CaCO_3$
$2\cdot6327w = $ Per cent. ferrous carbonate, $FeCO_3$

Success in this determination largely depends upon the speed at which the carbon dioxide is liberated. If the gas comes off too rapidly, some carbon dioxide may pass through the system without giving up its moisture to the desiccating agent.

Concentrated hydrochloric or nitric acid, or dilute sulphuric acid, may be used as indicated on page 624. Morgan [1] recommends orthophosphoric acid (sp. gr. 1·75) for decomposing the carbonates and then the addition of a moderate excess of chromic acid (3–4 grms.), whereby the carbon is oxidised. Thus carbon dioxide and carbon may be determined separately on the same sample. We have had no experience with this phosphoric acid process.

For minerals which decompose slowly with hydrochloric acid, e.g. scapolite, Borgström [2] recommends the addition of a little hydrofluoric acid to the hydrochloric acid. Though the glass is attacked, the flask can be used for a number of determinations; the results are said to be higher than when hydrochloric acid is used alone, because the mineral is more completely decomposed.

§ 306. The Volumetric Determination of Carbon Dioxide in Carbonates—Scheibler and Dietrich's Process.

The volume of the carbon dioxide obtained by the action of acids on carbonates can be measured quite accurately. A large number of instruments has been devised and modified for this purpose.[3] Scheibler's instrument is one of the oldest and, with some modifications, one of the best. Scheibler and Dietrich's instrument, illustrated in fig. 128, is fairly common.

The Apparatus.—In this apparatus, a measuring tube A is connected with a levelling tube B by means of a piece of thick-walled rubber tubing. A is graduated from 0 to 200 c.c.; B slides on the upright of the stand. The upper end of A is connected with a three-way cock d which connects A either with the air, or with the cooling coil C through which the gases pass on their way from the generating flask F to the measuring tube A. The coil C is immersed in a beaker of water at room temperature. A is filled with a 1 per cent. solution of boric acid. If all the connections are good, when the liquid in A is at zero, it will remain at zero if the levelling tube be depressed for some time, and then raised again.

[1] G. T. Morgan, *Journ. Chem. Soc.*, 85, 1001, 1904; E. C. Grey, *ib.*, 105, 2204, 1914; W. H. MacIntyre and L. G. Willis, *Journ. Ind. Eng. Chem.*, 7, 227, 1915.

[2] L. H. Borgström, *Zeit. anal. Chem.*, 53, 685, 1914.

[3] C. Scheibler, *Anleitung zum Gebrauch des Apparates zur Bestimmung des Kohlensauren Kalkerde in der Knockenkohle*, Berlin, 1862; *Chem. News*, 22, 75, 1870; R. Warington, *ib.*, 31, 253, 1875; E. Nicholson, *ib.*, 29, 245, 1874; H. Fresenius, *Zeit. anal. Chem.*, 19, 206, 1880; E. Dietrich, *ib.*, 3, 162, 1864; 4, 141, 1865; 5, 49, 1866; D. Sidersky, *ib.*, 25, 93, 1886; 26, 336, 1887; E. Jager and G. Krüss, *ib.*, 27, 721, 1888; R. Baur, *ib.*, 23, 371, 1884; A. Classen, *ib.*, 15, 288, 1876; F. Schulze, *ib.*, 2, 289, 1863; A. Gawalovski, *ib.*, 18, 244, 560, 1879; G. Burkhardt, *Neue Zeit. Rüb. Ind.*, 16, 115, 1886; D. Sidersky, *Zeit. Ver. Rüb. Ind.*, 20, 919, 1885; W. Borchers, *Journ. prakt. Chem.*, (2), 17, 353, 1878; G. Lunge, *Chem. Ind.*, 8, 166, 1885; F. Fuchs, *Chem. Ztg.*, 13, 873, 1889; C. Tubandt and H. Weisz, *ib.*, 46, 1105, 1922; R. Finkener, *Zeit. angew. Chem.*, 3, 273, 1890; W. Thorner, *ib.*, 2, 641, 1889; E. Cramer, *Tonind. Ztg.*, 18, 577, 1894; C. S. Robinson, *Soil Sci.*, 10, 41, 1920; A. Grégoire, J. Hendrick, E. Carpiaux and E. Germain, *Ann. Chim. anal.*, 18, 1, 1913.

Adjustment of the Apparatus.—When the instrument is connected up as in the diagram, read the barometer and thermometer. A table is supplied with the instrument. This gives half the amount of substance to be weighed out for all variations of temperature and pressure between $10°$ and $25°$, and 720 mm. and 770 mm. The right amount of the powdered substance [1] is weighed into the flask F, and a small tube a containing 5 c.c. of hydrochloric acid (sp. gr. 1·124) is placed in the same flask. The acid tube is reared against the side of the flask, so that the acid does not come in contact with the powder. The flask is closed by means of a rubber stopper. The liquid in A is set so that the lower level of the meniscus is at the zero of the scale when the liquid in the levelling tube is at the same level.

Evolution of Gas.—The generating flask is now tilted so that the acid comes in contact with the carbonate. When all action has ceased and the apparatus has cooled two or three minutes, the levels of the liquid in A and B are adjusted, and the lower level of the meniscus in A is read.[2] Add to this a correction for the volume of the carbon dioxide dissolved by the liquid in the generating flask F.[3] Half the sum represents the percentage amount of carbon dioxide in the given sample.

FIG. 128.—Scheibler and Dietrich's Apparatus.

§ 307. The Volumetric Determination of Carbon Dioxide in Carbonates— Lunge and Marchlewski's Process.

The apparatus just mentioned gives good results, but it has some weak points. Lunge and Marchlewski [4] have introduced several improvements, but their apparatus, shown in fig. 129, is somewhat expensive. Still, it is one of the best instruments for the purpose on the market.

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[1] As indicated in the table, multiplied by 2. The reason for varying the amount of sample with different temperatures and pressures is to avoid calculating the weight of gas corresponding with the volume measured in A.

[2] If, after the volume of the gas has been initially read, gas is still slowly evolved from the generating flask, magnesium carbonate is present.

[3] See S. Hatta (*Journ. Soc. Chem. Ind. Japan*, **36**, 8B, 1933) for the correction for the solubility of carbon dioxide and J. R. Branham (*Bur. Standards Journ. Research*, **12**, 353, 1934) for the loss of gas due to solution in rubber connections and lubricants. In O. Pettersson's method (*Ber.*, **23**, 1402, 1890) the carbon dioxide is driven from the generating flask by the simultaneous action of the acid on iron or aluminium wire. Carbon dioxide and hydrogen collect in the measuring flask. The former is determined in an Orsat's apparatus.

[4] G. Lunge and L. Marchlewski, *Zeit. angew. Chem.*, **4**, 229, 412, 1891; **6**, 395, 1893; W. Thörner, *ib.*, **2**, 644, 1889; R. Lorenz, *ib.*, **6**, 395, 411, 1893; M. A. von Reis, *Stahl Eisen*,

The Apparatus.—In the diagram (fig. 129) *A* is a flask (about 30 or 40 c.c. capacity) closed by a soft rubber bung. The bung is fitted with a dropping funnel *a* and a capillary tube bent at right angles, as shown in the diagram. *B* is the gas measuring tube, *D* is the levelling tube and *C* is a compensating tube whose function is described below. These tubes are connected by means of thick-walled rubber tubing and mounted as shown in the diagram. *E* is an Orsat's absorption pipette containing soda solution or potash.[1] The soda lime tube *F* protects the contents of the Orsat's pipette from atmospheric carbon dioxide. *G* and *H* are three-way stopcocks. The apparatus is used as follows:—

Adjustment of the Apparatus. —The decomposition flask *A* is cleaned perfectly free from acid, and an amount of substance which will give not more than 50 c.c. of carbon dioxide is weighed into the flask along with 0·08 grm. of thin aluminium wire.[2] Insert the bung and close the tap on the dropping funnel *a*. Raise the mercury in *B* until it reaches the stopcock *G*,[3] which is open to the air. Connect *A* and *B*, but not *E* and *B*, *via* the stopcock *G*. Depress the mercury in *B* by lowering *D* as far as possible. Turn the stopcock *G* so that when the levelling tube is raised the air in *B* will be driven out of the system. When the mercury reaches *G*, again connect *A* with
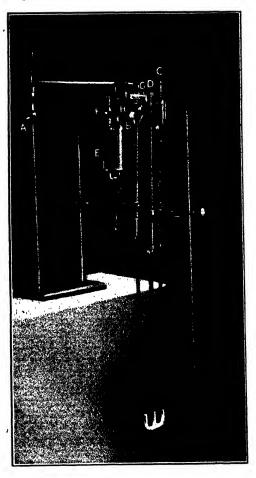
Fig. 129.—Lunge and Marchlewski's Apparatus.

B through stopcock *G* and repeat the operation three or four times so as partially to evacuate the vessel *A*.

Evolution of the Gas.—With the mercury in the levelling tube *D* lower than in *B*, and *A* and *B* in communication, add about 10 c.c. of hydrochloric acid (3 vols. water, 1 vol. acid) *via* the funnel *a*. Close the stopcock of the funnel just before the last drop of acid runs into the flask. Carbon dioxide is evolved

8, 257, 1887; O. Vogel, *ib.*, 11, 486, 1890; C. Reinhardt, *ib.*, 12, 648, 1040, 1891; G. Lunge, *Chem. Ztg.*, 12, 821, 1888.

[1] SODIUM HYDROXIDE SOLUTION.—104 grms. of ordinary caustic soda dissolved in 130 c.c. of water will make about 200 c.c. of a solution approximately 13N. See page 619.

[2] Weigh, say, one metre of the thin wire and calculate the length required to give 0·08 grm. Lengths cut this size can be kept in a bottle ready for use.

[3] This requires care, or mercury will be driven where it is not wanted.

at once. The mercury in B is depressed. Lower the levelling tube D so that, all the time, the mercury in D is lower than in B. The flask A is gently warmed with a spirit lamp for about 2 minutes. Add more acid and repeat the operation.[1] In this way nearly all the carbon dioxide is driven from the liquid in A by the escaping hydrogen. When all has dissolved, add dilute acid through the funnel a until the flask A, as well as the connecting tube, are filled almost as far as the stopcock G. Close stopcock G. Let stand for about 10 minutes so as to acquire the temperature of the room. Meanwhile the flask A and its connecting tube can be removed and cleaned.

Measuring the Volume of the Gas.—Adjust the levels of the mercury in C and D until the mercury in C is at the 100 c.c. mark, and at the same level in B. Now read the volume of the gas confined in B from the top of the mercury meniscus. Suppose it be 147·5 c.c. The level of the liquid in the Orsat's pipette E is adjusted by opening the three-way cock H, and blowing through the tube F until the soda solution stands at the etched mark just below the stopcock. Close the stopcock H. Let the mercury in the levelling tube stand at a higher level than in B. Connect B to the three-way cock H on the Orsat's pipette E. Now put B and E into communication with each other by turning cocks G and H and raise D gradually until the mercury in B is near the stopcock G. Then slowly depress D until the soda solution stands at its former level. Repeat this operation three times. The soda solution absorbs the carbon dioxide. The motions require care, because it is easy to get the soda solution into the measuring tube B, and mercury into the Orsat's pipette E. A little practice and attention will soon give control of the movements of the liquids. When the level of the soda solution is at its mark below the cock H, close the cocks H and G, and adjust C and D as before. Read the level of the mercury in B from the top of the meniscus. Suppose that 108·4 c.c. are indicated. The difference in the two readings represents the volume of carbon dioxide at 0° and 760 mm. pressure given off by the decomposition of the carbonate. We have:

Mercury level before	.	.	.	.	.	147·5 c.c.
Mercury level after	.	.	.	.	.	108·4 c.c.
Carbon dioxide absorbed .		.	.	.	.	39·1 c.c.

But one cubic centimetre of carbon dioxide at 0° and 760 mm. corresponds with 0·0019643 grm. of carbon dioxide, or 0·004468 grm. of calcium carbonate. Hence, 39·1 c.c. of carbon dioxide must correspond with $0·004468 \times 39·1$ grms. of $CaCO_3$. If 0·1787 grm. of whiting were used in the decomposition flask A, it follows that the whiting contained:

$$\frac{0·4468 \times 39·1}{0·1787} = 97·75 \text{ per cent. } CaCO_3$$

Amount of Carbonate required for an Experiment.—It will be observed that we selected a weight 0·1787, which is $2\frac{1}{2}$ times less than 0·4468. Hence, a considerable saving of time is effected by taking, as recommended by Lunge and Marchlewski:

Grams of substance taken.	Nature of the carbonate rock.	1 c.c. of CO_2 represents $CaCO_3$.
0·1787(2)	Very rich in carbonates	2·5 per cent.
0·2234	Marls rich in carbonates	2·0 per cent.
0·4468	Marls poor in carbonates	1·0 per cent.
2·2340	Minerals poor in carbonates	0·2 per cent.

[1] This can be done without admitting air.

If carbon dioxide, not calcium carbonate, be wanted, the factor 0·4468 must be changed to 0·19643, and a corresponding change made in the amount of materials taken for the analysis in order that the number of cubic centimetres absorbed may be a simple multiple or submultiple of the per cent. of carbon dioxide in the substance.

The Compensation Tube.—This is an ingenious device to render the reduction of the volume of the gas to the standard temperature and pressure unnecessary.[1] The compensation tube C contains a known volume of air such that it would occupy 100 c.c. at 0° and 760 mm. If the same temperature and pressure be applied to another gas, it also will take up a volume corresponding to 100 c.c. at 0° and 760 mm. If moist gases be in question, a drop of water is introduced into the compensation tube. From the well-known gas laws, it follows:

$$\text{Volume at } t° \text{ and } p \text{ mm.} = \text{Volume at } 0° \text{ and } 760 \text{ mm.} \times \frac{(273+t)760}{273(p-f)}$$

where f is the vapour pressure of water at the temperature t, as given from vapour pressure tables. To adjust the compensation tube, read the temperature t and barometer p. Find the corresponding value of f from the tables. Calculate the volume which 100 c.c. of gas at 0° and 760 mm. would occupy at $t°$ and $(p-f)$ mm. pressure. Adjust the levelling tube by means of the Göckel's stopcock [2] G until the level of the mercury in the compensation tube is at the required graduation. Close the Göckel's stopcock. The tube is then ready for use.

§ 308. The Dry Combustion Process for the Determination of Carbon.

One of the best methods for the determination of carbon is to heat the dry clay in a porcelain or fireclay boat in a combustion tube, in a current of oxygen, as is regularly done in the ultimate analysis of organic compounds. The carbon dioxide which is formed, and also the water, are determined by absorption in suitable vessels. For example, the water is absorbed in a weighed calcium chloride tube and the carbon dioxide in a weighed potash bulb. The increase in weight of the potash bulb represents the amount of carbon dioxide derived (1) from the carbonates in the clay and (2) from the combustion of the carbonaceous matter. The former is determined by another operation (pages 624 and 625), and the difference represents that produced by the combustion of the carbon.[3]

The operation is carried out as follows: A porcelain tube A (fig. 130), 2 ft. by 1 in., is used for the combustion and is heated preferably in an electric tube furnace B.[4] If the clay contains volatile carbonaceous matter, the forward portion of the tube is packed to within 3 ins. of the end with freshly ignited, wire-form copper oxide,[5] which is kept in position by loose plugs of ignited asbestos or by small rolls of well-oxidised copper gauze. In any case, the layer
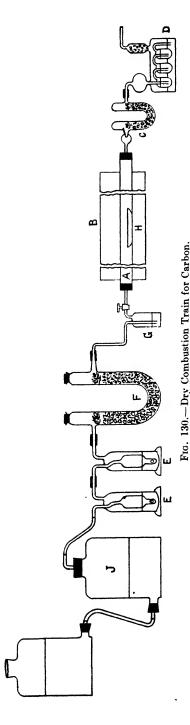
[1] See C. E. Millar, *Journ. Ind. Eng. Chem.*, 5, 234, 1913.
[2] H. Göckel, *Zeit. angew. Chem.*, 13, 961, 1238, 1900.
[3] Or the carbonates can be removed by digestion in dilute hydrochloric acid, washing and drying before combustion.
[4] Any of the standard types of gas-fired combustion furnaces can be used. The Hedley furnace (T. J. Hedley, *Journ. Chem. Soc.*, 119, 1242, 1921; *Journ. Soc. Chem. Ind.*, 42, 433T, 1923) is a convenient form.
[5] E. Erlenmeyer, *Zeit. Pharm.*, 6, 156, 1854; C. Reischauer, *Viert. prakt. Pharm.*, 11, 38, 1862; E. C. C. Stanford, *Chem. News*, 7, 81, 1863.

Fig. 130.—Dry Combustion Train for Carbon.

of copper oxide is a desirable precaution, since it ensures the complete oxidation of the carbon to the dioxide. The fore end of the combustion tube is fitted with a one hole rubber bung and the bulbiform side arm of a U-tube C is inserted through the hole until the end of the arm is just flush with the inner margin of the bung. The U-tube is filled almost to the level of its side arms with granular calcium chloride which has been sifted free from dust. Loose plugs of glass wool keep the calcium chloride in position. The open ends of the U-tube are closed by rubber bungs, or preferably are sealed off, after the tube has been charged.[1] The other side arm of the U-tube is connected by thick-walled rubber tubing to a weighed Landsiedl's potash bulb D, charged as indicated on page 619. The arms of the U-tube and the Landsiedl's bulb must be brought into contact with each other under the rubber sleeve so as to minimise any possible leakage of carbon dioxide at the joint.

The rear end of the combustion tube is connected through another rubber bung with a purifying and drying train [2] for the removal of carbon dioxide and moisture from the oxygen and air used in the combustion. An efficient form of train comprises two Muencke's gas washing bottles E, E and a large U-tube, F, 15 ins. high by $1\frac{1}{4}$ in. diameter, all connected in series. The bottles are one-third filled with a 10 per cent. solution of potassium hydroxide, while the rear limb of the U-tube is charged with granules of soda lime and the fore limb with granular calcium chloride. A 50 c.c. gas washing bottle G, with a glass tap fused to its exit arm, is interposed between the fore limb of the large U-tube and the combustion tube. 10 c.c. of concentrated sulphuric acid, placed in this bottle, give the oxygen a final drying and also indicate the rate at which the gas is passing through the system. The rate is

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[1] Note particularly footnote 3, page 619. Rubber bungs are liable to pick up dirt and grease during a determination, whereas a sealed limb can be wiped clean and is entirely gas-tight.

[2] E. Sauer, *Zeit. anal. Chem.*, **31**, 195, 1892; F. Bohm, *Chem. Ztg.*, **27**, 1037, 1903.

controlled by the glass tap and by fusing a glass lever to one of its arms a very fine adjustment is obtainable.

To carry out a determination about 5 grms.[1] of the dry (110°) clay are weighed out into a clay or porcelain combustion boat H, which has been previously ignited, and the absorption bulb D is also weighed.[2] The bulb and boat are placed in their respective positions in the system, as shown in fig. 130, and oxygen is admitted from the aspirator J so that one to two bubbles per second pass the Landsiedl's bulb. The current through the furnace is then turned on and adjusted by an external resistance so that the furnace reaches a temperature of about 1000° in three-quarters of an hour; the temperature is then maintained at this value by a suitable increase in the external resistance.[3] In about another 45 minutes the carbon in the clay will have been completely combusted. Owing to the difference in the densities of air and oxygen, the oxygen must be swept out of the potash bulb before weighing. Hence replace the aspirator J by an aspirator containing air and pass a slow stream of air through the system for 20 minutes. Then disconnect, cool and weigh the Landsiedl's bulb.

Errors.—Chlorine compounds are a source of error since on combustion some or all of the chlorine will be eliminated as such and absorbed in the potash solution, thus increasing the apparent amount of carbon in the clay. When chlorine is present, the clay is mixed with lead chromate (free from carbonates, acetates and nitrates) before it is heated in the current of oxygen.[4] The lead chromate absorbs the chlorine and also some carbon dioxide.[5] The amount of the latter is determined by the method of page 624 or 625. The remainder of the carbon dioxide is given by the increase in weight of the potash bulb. Alternatively a roll of silver gauze can be inserted at the fore end of the combustion tube, in front of the layer of copper oxide. The gauze must not be heated strongly, but only kept warm, since the silver halides are volatile at higher temperatures.

Sulphur compounds in the clay introduce a similar source of error to chlorine compounds as the oxides of sulphur, formed on combustion, are absorbed in the potash bulb. In such cases the combustion must be carried out with lead chromate as described above.

If the clay contains quartz grains in which calcite is included, these grains will be disrupted on dry combustion owing to the decomposition of the calcite, whereas they will be unaffected by the wet combustion process. Thus, in such cases, the reported percentage of carbon will be higher by the former than by the latter process.[6]

§ 309. The Analysis of Carborundum.

Grinding the Sample.—Carborundum is so hard that it is impossible to grind it to a fine state of subdivision without a comparatively large amount of contamination (page 103). Again, this substance is so resistant to ordinary

[1] The amount of clay taken is necessarily conditioned by the amount of carbon it contains.

[2] See pages 621 and 622.

[3] The furnace should be "calibrated" before use by inserting a thermo-couple in the empty combustion tube and noting (1) the rates of rise of temperature for varying external resistance, and (2) the external resistance necessary to maintain the furnace at any given temperature.

[4] See footnote 2, page 635. H. Ritthausen, *Zeit. anal. Chem.*, **22**, 107, 1883; N. N. Ljubavin, *Zurn. russk. Fig. Chim.*, **14**, 480, 1887.

[5] Compare J. Lindner, *Ber.*, **59B**, 2561, 1926.

[6] E. C. Shorey and W. H. Fry, *Journ. Ind. Eng. Chem.*, **9**, 588, 1917. For errors in the determination of carbon, see E. Coffari, *Gazz. Chim. Ital.*, **63**, 323, 1933.

chemical reagents that it must be very finely ground if it is to be completely decomposed.[1] Mühlhäuser[2] has shown that, the coarser the powder, the greater the error in the determination of the carbon, presumably owing to incomplete combustion.   He stirred the powdered material in 2 litres of distilled water and, after settling 1 minute, poured off the liquid with carborundum in suspension.   This he stood for 5 minutes and then again poured off the liquid.   The water contained the so-called 5-min. powder; the 1-min. powder remained as a residue.   The stuff which settled after standing 1 minute was reground and again suspended in water.   The sample was thus reduced to powders so fine that they remained suspended in water after standing respectively 1 and 5 minutes.   These operations are obviously laborious and occupy a long time—more than a day.

When an abundant supply of the material is available in sufficiently large blocks, as at a plant where carborundum is manufactured, the sample is ground by hand, until it passes a 150's mesh, in a mortar and pestle roughly shaped from the same block of carborundum as that under analysis.   There is thus no possibility of extraneous contamination.   When this procedure is impracticable, the sample is first pulverised in an Abich's pestle and mortar (fig. 38) and then ground to the required degree of fineness in a steel mortar (fig. 39).   The iron, abraded from the mortars and pestles, can be removed magnetically as indicated on page 104 or, alternatively, the powder can be digested with diluted hydrochloric acid to dissolve the iron, followed by washing and drying.   The possibility must be borne in mind that either treatment may result in the removal of certain portions of the mineral together with the iron, thus giving a misleading analysis.

The Determination of Carbon.—The carbon of carborundum and silicon carbides cannot be burned off completely even in a stream of oxygen, although it can be oxidised by fusing the sample with lead chromate (Mühlhäuser, Moissan); red lead (Johnson); lead monoxide (Schwarz); lead peroxide; bismuth tetroxide, Bi_2O_4 (Brearley, Norton); or a mixture of potassium carbonate and nitrate (Moissan).[3]

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[1] Phosphoric acid (sp. gr. 1·75) at 230° decomposes carborundum completely in 3 hours —M. Wunder and B. Jenneret, *Compt. rend.*, 152, 1770, 1911.

[2] O. Mühlhäuser, *Zeit. anal. Chem.*, 32, 564, 1893.

[3] O. Mühlhäuser, *Zeit. anal. Chem.*, 32, 564, 1893; H. Wdowiszewski, *Chem. Ztg.*, 34, 1209, 1910; R. Amberg, *ib.*, 34, 904, 1910; C. M. Johnson, *Journ. Amer. Chem. Soc.*, 28, 862, 1906; H. Moissan, *Compt. rend.*, 117, 425, 1893; F. Foerster, *Zeit. anorg. Chem.*, 8, 274, 1895.   The powder may explode with lead chromate and potassium dichromate (W. Mayer's mixture, *Liebig's Ann.*, 95, 204, 1880).   H. Schwarz, *Dingler's Journ.*, 169, 284, 1863. A. Goetzl (*Chem. Ztg.*, 26, 967, 1902) heats the sample with an excess of lead oxide out of contact with air.   If more metallic lead is obtained than is required by theory, the sample contains an excess of graphite; and if less, an excess of sandy matters.   The carbon dioxide formed during the combustion can be absorbed and weighed.   G. Chesneau (*Ann. Chim. anal.*, 13, 85, 1908) heats a gram of the finely powdered sample to redness for 2 hours in a muffle—loss in weight represents free carbon.   Digest the residue with 20 c.c. of hydrofluoric acid and 1 c.c. of sulphuric acid on a sand bath.   Boil with hydrochloric acid, add hot water, wash by decantation and collect on a filter.   Ignite and weigh the residue as carborundum. A. L. Queneau, *Chem. Met. Eng.*, 9, 441, 1911; H. de Nolly, *Rev. Met.*, 8, 391, 1911; H. Brearley, *Chem. News*, 84, 23, 1901; F. H. Norton, *Refractories*, New York, 514, 1931.   For the alleged carbonaceous impurities in red lead, see H. Brearley, *Chem. News*, 84, 23, 59, 1901; J. G. McIntosh, *ib.*, 84, 46, 1901.   H. Moissan, *Compt. rend.*, 117, 425, 1893; O. Hönigschmid, *Karbide und Silizide*, Halle a S., 92, 1914.   S. W. Parr (*Journ. Amer. Chem. Soc.*, 30, 764, 1908) heats together in a Parr's bomb 1 to 2 parts of "boro-magnesium mixture" (boric acid 5 parts; potassium nitrate 4 parts; and magnesium 1 part, all finely powdered) with 10 parts of sodium peroxide and 0·3 to 0·5 part of finely powdered carborundum.   The fused mass contains the carbon as carbonate.

A thoroughly clean and dry combustion tube of hard glass [1] is fitted with one-hole rubber stoppers. A plug of ignited fibrous asbestos about 1 cm. long, and about 5 cm. from the end, is placed in the tube. Fill 15 cm. of the tube with coarsely granular lead chromate.[2] Then mix 0·2 to 0·3 grm. of the powder under investigation with 20 times its weight of powdered lead chromate and transfer the mixture to the combustion tube. Then fill up the tube to within 5 cm. from the other end with more granular lead chromate. Insert another centimetre plug of ignited asbestos. Connect the left hand end of the tube (fig. 131) through an efficient drying train to an aspirator containing

Asbestos Plug ← Lead Chromate ← Substance and Lead Chromate → ← Lead Chromate → Asbestos Plug

Fig. 131.— Diagrammatic Sketch of Combustion Tube.

oxygen (fig. 130). Gently tap the tube so that a channel is left above the powder for the passage of gas. Connect the other end of the tube [3] to the weighed absorption train (fig. 130). Test the apparatus to see that all the joints are gas-tight. Adjust the tap on the drying train so that oxygen passes through the system at the rate of 2 or 3 bubbles per second. Light the burners [4] on the extreme right to within 10 cm. of the powdered substance, with the flame high enough just to warm the tube. Now light the first few burners on the extreme left of the tube and then gradually increase the heat from either end of the furnace towards the centre so that the temperature of the layer of powdered lead chromate and substance is slowly raised. Increase the speed of the oxygen towards the end of the analysis. The speed should never be greater than will permit the bubbles to be easily counted.[5] When the tube is dull red and all the moisture has been driven into the calcium chloride tube,[6] lower the height of the flames and in about 5 minutes extinguish them. Replace the current of oxygen by a current of air. In about 20 minutes, remove the potash bulbs and the calcium chloride tube, and in about half an hour weigh them. The increase in weight of the potash bulbs represents the carbon dioxide formed by the combustion of the free and combined carbon in the given sample. Multiply the result by 0·2727 to get the amount of carbon equivalent to the carbon dioxide absorbed in the potash bulbs. The increase in weight of the calcium chloride tube represents the combined hydrogen and the water in the given sample. The carbon is usually a little low and the water a little high.[7]

The Determination of the Silica.—The silica is determined by fusing the

[1] Inside diameter 13 mm., walls 1–1½ mm. thick, length depends upon the furnace. The tube should project 5–8 cm. from each end of the furnace. The sharp ends of the tube should be rounded in the flame. The tube should be dried by passing a current of clean dry air through the warm tube. In drying tubes by a blast of air, dust must be removed from the air by a suitable filter—A. B. Dixon, *Chem. News*, 59, 308, 1889.

[2] Ignited at a *dull red* heat just before use and cooled in a desiccator.

[3] An asbestos plate is generally fitted over the end of the combustion tube near the calcium chloride tube.

[4] Gas-fired furnaces (see footnote 4, page 631) are preferable in this operation as the heated section of the tube cannot be inspected in an electric tube furnace, and it is essential that the lead chromate (m.p. *c.* 840°) should not be heated above a dull red heat, otherwise it will attack the glass walls of the combustion tube.

[5] About 4 bubbles per second—G. Auchy, *Journ. Amer. Chem. Soc.*, 24, 1206, 1902.

[6] Assisted, if necessary, by the cautious application of a small spirit flame at the end of the combustion tube near the calcium chloride tube. Be careful not to heat the stopper.

[7] R. de Roode, *Amer. Chem. Journ.*, 12, 226, 1890.

powder[1] with sodium carbonate as for clays; or by fusing with sodium peroxide.[2] The time required for the fusion is much longer than for clays[3] and it is necessary to watch for any undecomposed powder in the residue remaining after the fused mass has been taken up with water and acid. If any be present, a re-fusion of the undecomposed residue is necessary.[4] The solution obtained from the sodium carbonate fusion is treated exactly as described for clays (page 147).

Very few investigations have been made on the analysis of carborundum and silicon carbides. We sometimes have to deal with silicon carbide present in old graphite crucibles,[5] and with carborundum admixed with clay in compounding certain bodies. In that case, Mühlhäuser's method of grinding must be rejected. The 1-min. powder has a different composition from the 5-min. powder. The grinding need not be so protracted if the alkalies have not to be determined.[6] The substance may then be first broken in a hard steel mortar, and finished with an agate mortar and pestle. 0·5 grm. may be calcined for loss on ignition[7] in a platinum crucible. A crucible with 1 grm. of powdered carborundum weighed 27·9834 grms. After 20 minutes' calcination over a Bunsen burner, the whole weighed 27·7413 grms.; after another 12 minutes' calcination, 27·7390 grms.; after 25 minutes' further calcination on the blast, 27·7398 grms.; after 20 minutes' more blasting the weight was 27·7415 grms. No marked change in weight occurred with a more prolonged blasting. The increase was probably due to oxidation of ferrous oxide (page 136). The calcination for loss on ignition is to be conducted over a Bunsen burner until no further loss in weight occurs. A known weight of the previously ignited sample (see footnote 7) is mixed with 5 to 6 grms. of red lead,[8] or lead carbonate, and a gram of sodium nitrite. The mixture is fused over a small Méker burner to ensure oxidising conditions. When

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[1] Mühlhäuser (*l.c.*) separates the sample into 1-min. and 5-min. powders. The latter is used for the carbon determination, the former for the silica determination.

[2] For Parr's boro-magnesium fusion mixture see footnote 3, page 634. F. H. Norton (*Refractories*, New York, 515, 1931) fuses 0·5 grm. of the sample with 5 grms. of sodium carbonate and 4 grms. of sodium peroxide in a nickel crucible.

[3] Fusion of the 150's mesh powder for 2 hours is recommended.

[4] The reaction is sometimes represented by the symbols: $SiC + Na_2CO_3 \rightarrow Na_2SiO_3 + 2C$. Hence, if a dark-coloured residue remains, it does not necessarily mean undecomposed powder. It may be unburnt carbon. The suspended undecomposed matter is filtered off, washed, calcined in a platinum crucible and re-fused with sodium carbonate. The cooled mass is taken up with water and acid and mixed with the main portion.

[5] Formed in the body of the crucible itself while in use. For the determination of graphitic silicon in siliceous residues, see L. H. Callendar, *Analyst*, 58, 580, 1933.

[6] Which is not usually the case. Wdowiszewski (*l.c.*) puts for his final analysis: "$K_2O + Na_2O$ + analytical errors 1 per cent."

[7] Note the difficulty with "loss on ignition" owing to the fact that silicon carbides scarcely burn even in a current of oxygen. The object of the ignition is to burn off as much of the carbon as possible in order to prevent the reduction of the lead oxide to metallic lead, which would ruin the platinum crucible. If alkalies are to be determined, the sodium nitrite must necessarily be omitted.

[8] The red lead must be specially purified, or a blank analysis made so as to be able to correct the final product for silica, alumina, etc. If the red lead contains particles of metallic lead, it will spoil the platinum crucible. The red lead is conveniently made by treating an aqueous solution of pure lead nitrate with a saturated solution of oxalic acid containing 3 per cent. of nitric acid. The precipitate is separated, washed, dried and ignited at a dull red heat for some hours. Lead carbonate is made by precipitating a solution of lead acetate with the calculated amount of ammonium carbonate. If the sample under investigation contains organic matter, the carbon should be destroyed by gentle ignition. A. F. Crosse (*Journ. Chem. Met. Min. Soc. S. Africa*, 2, 182, 1897; *Chem. News*, 76, 253, 1897), in "assaying graphite crucibles," mixes the material with enough manganese dioxide to burn all the graphite.

the melt is clear, cool the hot crucible with its lid in position by plunging the hot crucible in cold distilled water. The cake is usually easy to loosen with dilute nitric acid (not hydrochloric acid). Transfer the mass to an evaporating basin and evaporate with concentrated nitric acid to dryness. The fragments gradually soften and they can be rubbed with an agate pestle from time to time. The dry mass is treated for silica, as described for clays, but nitric acid is used in place of hydrochloric acid. The filtrate is treated in the cold with hydrochloric acid in order to precipitate most of the lead as chloride. Filter off the lead chloride and wash with hydrochloric acid (1 : 1). Evaporate the filtrate to dryness and take up the residue with hydrochloric acid (1 : 4). Saturate the solution with hydrogen sulphide. Filter off the lead sulphide. Boil the filtrate to expel the hydrogen sulphide. The alumina may then be determined in the solution in the usual manner (page 164).

The Estimation of Silicon Carbide—SiC.—There is a difficulty in calculating the amount of silicon carbide from the analytical data. For instance, suppose that the analysis gives :

	Per cent.
Silica	48·34
Carbon	50·12
Alumina and ferric oxide	16·07
Magnesia	0·53
Lime	1·02
Potash	0·21
Soda	0·09
Total	116·38

This result assumes that all the silicon is present as silica. Part is present as silicon carbide, presumably SiC. It is assumed that if the amount of silicon, present as silicon carbide and as silica, had been determined, the total would have been 100 instead of 116·38. Part of the oxygen which we have supposed to be combined in the silica was not present in the given sample. Since 32 parts of oxygen correspond with 60 parts of silica, 16·38 parts of oxygen correspond with 30·71 parts of silica.[1] Hence, 48·34 − 30·71 = 17·63 per cent. of free silica. Again, 60 parts of silica correspond with 40 parts of silicon carbide—SiC; hence, 30·71 parts of silica correspond with 20·47 parts of SiC. Again, 40 parts of silicon carbide correspond with 12 parts of carbon; hence, 20·47 parts of silicon carbide correspond with 6·14 parts of carbon as silicon carbide. Hence, 50·12 − 6·14 represents 43·98 per cent. of free carbon. The first two terms of the preceding analysis may now be revised. They read :

Silica	17·6
Silicon carbide	20·5
Carbon	44·0

The collected errors in the analysis are here distributed between the silica, silicon carbide and the carbon, and the method can only be regarded as a method of approximation.

According to Parr,[2] the free silica is removed by evaporation with hydrofluoric acid, which does not attack silicon carbide—SiC. Hence, determine the total silicon by the fusion process and the free silica in a separate sample

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[1] It will be noted that we use rounded atomic weights. The resulting error is negligibly small in comparison with the approximate nature of the method of computation.
[2] S. W. Parr, *Journ. Amer. Chem. Soc.*, 30, 764, 1908.

by means of hydrofluoric acid.[1] He expresses the analysis : silica (volatilised with HF), 8·27; metallic iron (removed by a magnet), 4·37; silicon as Si (by fusion process), 63·58; carbon, 23·67 per cent.

§ 310. The Analysis of Siloxicon.

Siloxicon is a greenish-grey refractory substance which varies in composition between Si_2C_2O and Si_7C_2O. It is vigorously decomposed, but not completely, by a fused mixture of sodium carbonate and potassium nitrate. Hydrofluoric and sulphuric acids have but a slight action. It is vigorously attacked by heated lead peroxide.[2] Spielmann[3] analysed a sample of the substance in the following way:-

Silicon, Carbon and Moisture. -The amount of moisture is determined, in the usual way, by drying the sample to a constant weight at 110°. The substance is "opened" by fusing the sample with sodium peroxide in a nickel crucible (page 264). The siloxicon is vigorously attacked and the cake, when cold, is digested in water and then with dilute hydrochloric acid. The resulting solution is treated in the usual way, and the amount of silica obtained is multiplied by 0·4672. This represents the amount of silicon · Si -- in the given sample. The total carbon is determined by fusing the sample with sodium peroxide in an iron boat in a combustion tube in a gentle stream of oxygen. In one experiment a potash bulb was fitted to the tube to collect any carbon dioxide which might escape; but none did escape and hence the carbon was afterwards estimated from the amount of carbonate in the product of the fusion of the siloxicon with the sodium peroxide in a crucible. The carbon dioxide in the fused mass was determined by the action of dilute sulphuric acid[4] in the usual way (page 624).

Alumina, Iron and Si_2C_2O.—Another sample was heated in a stream of chlorine in a porcelain boat in a hard combustion tube, whereby silicon tetrachloride, ferric chloride and a trace of aluminium chloride were volatilised. These were absorbed by passage (1) over the surface of water in a flask; and (2) through a U-tube loosely packed with cotton-wool. The silicon tetrachloride was hydrolysed to silicic acid. When all the ferric chloride had volatilised, the combustion tube was heated by the blast to as high a temperature as the tube would stand without collapsing. The reaction is at an end when the contents of the boat cease to glow. The cotton-wool was burnt in a crucible and the oxides of silicon and iron remained. The aluminium, iron and silicon collected in the flask and by the cotton-wool were determined as usual. The residue in the boat was heated in a current of oxygen and the carbon dioxide determined by absorption in potash bulbs. The final residue in the boat was found to be almost pure Si_2C_2O.[5]

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[1] E. W. Cheeseborough (*Chemist-Analyst,* 20, No. 4, 7, 1931) determines the total silicon in carborundum by fusing the sample with 10 times its weight of fusion mixture. The silicon as silicon carbide is determined by first treating the sample with sulphuric-hydrofluoric acid mixture and then fusing the residue with sodium carbonate, containing 2·5 per cent. of potassium nitrate.

[2] P. Jannasch and H. J. Locke, *Zeit. anorg. Chem.,* 6, 168, 321, 1894; A. Leclerc, *Compt. rend.,* 125, 893, 1897; P. Jannasch, *Zeit. anorg. Chem.,* 8, 364, 1895; *Chem. News,* 72, 51, 1895.

[3] P. E. Spielmann, *Journ. Soc. Chem. Ind.,* 24, 654, 1905.

[4] If hydrochloric acid be used, some chlorine will be formed.

[5] A portion of the sample was boiled with hydrofluoric acid. The filtrate contained a trace of ammonium silicofluoride. This was probably due to the presence of a trace of silicon nitride in the original sample.

Calculations.—Spielmann collects his results in the following manner:

	Per cent.
Total silicon (Na_2O_2 fusion)	50·31
Total carbon (Na_2O_2 fusion)	31·39
Iron (heating in chlorine)	1·07
Aluminium (heating in chlorine) and Nitrogen .	traces
Moisture	0·19
	82·96

Oxygen (difference from 100)	17·04
Residue in boat (Si_2C_2O) . . .	71·39
Carbon on heating chlorine residue in oxygen .	11·79

He interprets the analysis as follows:

Si_2C_2O	71·39
$SiCO_3$	10·81
SiC (carborundum)	5·81
Graphite	10·06
Fe	1·07
Volatiles	0·19
Al_2O_3; Si_3N_4 (by diff.)	0·67

The method of calculation [1] can only be regarded as the roughest of approximations.

§ 311. The Analysis of Graphite and Graphite Crucibles.

If the sample has no chemically combined water, as is the case with some of the artificial graphites, the carbon can be simply determined by heating the dried sample in a capacious Rose's crucible fitted so that a current of dry oxygen can be passed into the crucible while the calcination is in progress. The loss in weight represents the graphite burnt.[2] With natural graphites, however, this method is risky, because some silicates may be present which lose water only at elevated temperatures. Again, if pyrites, FeS_2, be present, the sulphur is burnt to the dioxide and ferric oxide is formed such that one part of pyrites furnishes two-thirds its weight of ferric oxide. If appreciable quantities of occluded oxygen, hydrogen, nitrogen and sulphur [3] be present, this method will give erroneous results.[4]

Berthier's old process [5] is not infrequently used when rapid work is needed.

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[1] Details are not given here as, apparently, there is an error in the figures quoted in the original paper.

[2] E. Donath, *Der Graphite*, Wien, 163, 1904. For the analysis of graphite, see E. Donath and A. Lang, *Stahl Eisen*, **34**, 1757, 1848, 1914; **35**, 870, 1915; A. Lang, *Oesterr. Chem. Ztg.*, **18**, 101, 1915. See also page 615, § 300.

[3] For the determination of sulphur in graphite, see L. Harant, *Zeit. angew. Chem.*, **44**, 921, 1931; K. Swoboda, *ib.*, **45**, 49, 1932.

[4] E. Donath, *Der Graphite*, Wien, 168, 1904; G. Auchy, *Journ. Amer. Chem. Soc.*, **22**, 47, 1900.

[5] P. Berthier, *Dingler's Journ.*, **58**, 391, 1835; *Traité des Essais par la Voie Sèche*, Paris, **1**, 222, 1847; W. F. Gintl, *Zeit. anal. Chem.*, **7**, 423, 1868; G. C. Wittstein, *Dingler's Journ.*, **216**, 45, 1875. G. Forchhammer (*Berg. Hütt. Ztg.*, **5**, 465, 1846) recommended a mixture of three parts of lead monoxide and one part of lead chloride in place of lead monoxide alone, because the former fuses at a lower temperature and does not corrode the crucible so much. A. Schrötter (*Dingler's Journ.*, **116**, 115, 1850) used lead oxychloride.

0·5 grm. of the finely powdered sample is intimately mixed with 12 grms. of powdered lead monoxide and placed in an unglazed porcelain crucible. The surface of the mixture is covered with 12 more grms. of lead monoxide and the crucible heated slowly. The lead monoxide is reduced by the carbon so that 1 grm. of reduced lead represents 0·029 grm. of graphite or, otherwise, 0·2727 grm. of graphite is represented by a loss in weight of 1 grm. Quite good results can be obtained by this process if care be exercised in selecting the lead monoxide and if the sample be free from sulphides.

The sample can be readily powdered in a hardened steel mortar with a ball pestle (fig. 39), and finished in an agate mortar. The wet combustion process
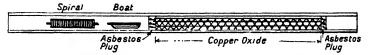
FIG. 132.—Diagrammatic Sketch of Combustion Tube.

gives rather low results.[1] Hence it is best to determine the carbon by the dry combustion process as given on page 634. The following modifications are desirable. Mix 0·2 to 0·3 grm. of the powdered sample with a generous excess of ignited powdered copper oxide[2] and transfer the mixture to the porcelain boat. Insert the boat in the combustion tube and, at a short distance behind it, place a roll of oxidised copper gauze, 13 cms. long, bound with copper wire arranged with a hook at one end. The roll should slide easily into the combustion tube[3]—see fig. 132. The lead chromate is replaced by copper oxide. The combustion is conducted as indicated on page 635.[4] When silicon carbides are absent, the loss on ignition,[5] silica, etc., can be determined as for clays.[6]

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[1] J. Widmer, *Zeit. anal. Chem.*, **29**, 160, 1890; *Chem. News*, **62**, 274, 1890. J. Goldstein, (*Chem. Ztg.*, **35**, 1134, 1911) considers that the combustion with sulphuric and chromic acids in a Corleis' flask, page 616, gives best results.

[2] S. S. Sadtler (*Journ. Franklin Inst.*, **144**, 201, 1907) mixed powdered graphite with an accurately weighed quantity of ignited magnesium oxide to prevent the fusion or agglomeration of the ash while the graphite was being ignited in a slow current of oxygen in a crucible. F. Browne (*Chem. News*, **98**, 51, 1908; **100**, 12, 1909) estimates carbon in graphite by ignition of a weighed sample with ferric oxide. The latter is at first reduced, but is afterwards oxidised, so that it remains at the end of the combustion the same as at the beginning. Hence the loss in weight represents the carbon.

[3] The copper gauze should be heated in a Bunsen flame so as to burn off oil and combustible matters. E. Calberia (*Journ. prakt. Chem.*, (1), **104**, 232, 1869) prefers silver gauze.

[4] The tube should be heated in a current of oxygen before the boat is introduced in order to burn out every particle of dust and remove all moisture.

[5] F. Stolba, *Dingler's Journ.*, **198**, 213, 1870. Due allowance must be made for the carbon.

[6] F. Mayer (*Chem. Ztg.*, **35**, 1024, 1911) estimates the amount of carbon in graphite from its calorific power. For the volumetric determination of carbon in graphite, see E. S. von Bergkampf and L. Harant, *Zeit. angew. Chem.*, **43**, 333, 1930.

CHAPTER XXXIX.

THE DETERMINATION OF WATER.

§ 312. Brush and Penfield's Method.

IT is sometimes desirable to determine directly the amount of water evolved when clays and related materials are ignited, although the determination is seldom asked for in industrial work. Brush and Penfield[1] conduct the process in the following way:—One or two bulbs are blown on a piece of hard glass combustion tube about 25 cm. long, with an internal diameter of about 0·6 cm., as shown in the diagram, fig. 133. Air is blown through the hot tube by means of a piece of glass tubing reaching nearly to the bottom of the combustion tube so that the tube may be thoroughly dried. Weigh the tube with its support.[2] Introduce about 0·5 grm. of the powdered sample by means of a thistle funnel, a, fig. 134,[3] without soiling the tube away from the closed end. The powder should occupy 2 or 3 cm. of the tube. Weigh the tube,
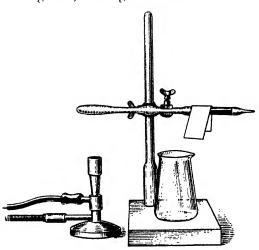
FIG. 133.—Determination of Water—Penfield's Process.

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[1] G. J. Brush, *Amer. J. Science*, (1), **46**, 240, 1868; S. L. Penfield, *ib.*, (3), **48**, 31, 1894; *Zeit. anorg. Chem.*, **7**, 22, 1894; F. A. Gooch, *Amer. Chem. Journ.*, **2**, 247, 1880; W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **700**, 77, 1919; W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, New York, 690, 1929. K. I. Viskont and I. P. Alimann (*Trans. Inst. Econ. Mineral Met.*, Moscow, No. 40, 1928; *Zeit. anal. Chem.*, **79**, 271, 1929) modify the process when determining the water in micas as follows: 0·3 grm. of the sample is weighed in a platinum boat, a few crystals of potassium chlorate are added and the whole covered with a layer of pure sodium tungstate. The boat is placed in a Penfield tube, and in front of it is inserted a plug of spongy asbestos and another of granulated lead oxide, wrapped in platinum gauze, to retain volatile constituents such as fluorine. Compare S. B. Kuzirian, *Amer. Journ. Sci.*, (4), **36**, 401, 1913. For a general study of the subject, see G. N. Huntley and J. H. Coste, *Journ. Soc. Chem. Ind.*, **32**, 62, 1913; J. A. P. Cresfield, *Journ. Franklin Inst.*, **172**, 495, 1911; E. H. Archibald and J. N. Lawrence, *Journ. Ind. Eng. Chem.*, **4**, 258, 1912; M. Dittrich, *Zeit. anorg. Chem.*, **78**, 191, 1912; P. Schläpfer, *Zeit. angew. Chem.*, **27**, 52, 1914.

[2] For a brass tube support for weighing on the balance pan, see fig. 1a, page 5.

[3] Can be made from a small pipette.

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support and sample together. Take care not to roll the powder in the tube towards the bulbs.[1] The open end of the tube is fitted with a piece of rubber tube holding a glass tube drawn out to a capillary end, b, fig. 134. Tap the tube so as to form a free passage for steam and gases above the powder. Support the tube with a very slight slope downwards from the closed end; wrap a strip of filter-paper or cloth about the bulb and tube near the open end —fig. 133. Keep the filter-paper moist and cold so as to ensure condensation

FIG. 134.

of the moisture expelled from the powder. The powder is now heated gradually up to the full heat of the burner. If the heated end tends to sink, turn the tube around from time to time.[2] In about 15 minutes, drive any water from the closed end of the tube a safe distance into the bulbs and draw off the closed end in a blowpipe flame. Let the portion of the tube containing the water cool in a horizontal position. When cold, wipe the outside clean [3] and weigh. Blow the moisture from the weighed tube by placing a small tube inside it and reaching to the bottom. The loss in weight represents the total moisture. The weighings are recorded as given in the following example:

Weight of tube plus powder	69·9214 grms.
Weight of empty tube	69·4321 grms.
Weight of powder	0·4893 grm.
Weight of portion containing water . .	20·8242 grms.
Weight after expulsion of water . .	20·7997 grms.
Weight of water	0·0245 grm.

Hence the sample contained 5·01 per cent. of water.

§ 313. Jannasch's Process for Water.

Jannasch [4] determines the moisture in the presence of sulphur and fluorine by fusing the substance with about six times its weight of lead oxide and collecting the water evolved in calcium chloride tubes. The other gases are said to be retained by the lead oxide. A hard glass tube, 26 cm. long, with an

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[1] If the sample has not been dried, it may now be dried at, say, 109° and the system weighed again for "water lost at 109°."

[2] For minerals like talc which do not give up all their water even when blasted, Penfield uses a cylinder of platinum foil (about 0·07 mm. thick) sprung tightly inside the part of the glass tube which is to be heated intensely, so as to prevent the glass squatting. The outside of the tube is surrounded with a piece of asbestos board. The end of the tube to be heated is partly surrounded with blocks of charcoal and fireclay so arranged that the tube is in a small furnace, which, later on, can be heated by a blast gas blowpipe.

[3] Beware of electrification of the tube on wiping.

[4] P. Jannasch, *Praktischer Leitfaden der Gewichtsanalyse*, Leipzig, 357, 1904; P. Jannasch and P. Weingarten, *Zeit. anorg. Chem.*, 8, 352, 1895; P. Jannasch and J. Locke, *ib.*, 6, 168, 174, 1894; M. Dittrich and W. Eitel, *ib.*, 75, 373, 1912; 77, 365, 1912; *Sitzber. Heidelberger Akad. Wiss.*, 19, 1911; W. Eitel, *Die Bestimmung des Wassers in Silikat-Mineralien und Gesteinen*, Frankfurt a. M., 1912; M. Dittrich, *Zeit. anorg. Chem.*, 78, 191, 1912; A. Faber, *Zeit. angew. Chem.*, 42, 406, 1929.

internal diameter of 1 cm., has a long bulb, *A*, blown about 11 cm. from one end. The bulb must have thick walls, and the whole tube be thoroughly dried. In fig. 135, *c* is a loosely packed layer of lead dioxide and lead monoxide (page 618) about 5 cm. long, kept in position by plugs of glass-wool *b, b*. The object of the lead oxides is to retain the chlorine, fluorine and sulphur. This part of the tube must be kept hot while an experiment is in progress.

From 0·5 to 1 grm. of the powder is mixed with six times its weight of lead monoxide [1] on glazed paper and the mixture is transferred to the middle of
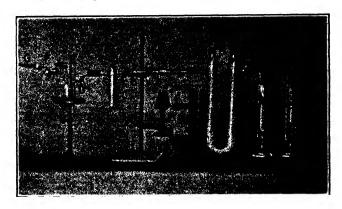
Fig. 135.—Direct Determination of Water.

the bulb *A* by means of a long strip of glazed paper and a feather. The operation requires care. No powder must be lost and none left sticking to the sides of the tube.[2] The right hand end of the tube is connected to a Sauer's drying train, *B, H, H* (page 632), for the removal of moisture and carbon dioxide from the aspirated air. The other end of the tube is attached to a weighed calcium chloride tube *C* and a weighed potash bulb *D* with its calcium chloride tube *E*. *F* is a guard tube which is connected to the aspirator *via G*.

Aspirate a *slow* current of air through the system and then raise the temperature of the bulb and contents gradually and finally finish the ignition at a full red heat. The calcium chloride absorbs the water; [3] the potash, the carbon dioxide. After about 10 minutes' ignition the reaction should be completed. Let the tube cool in a current of dry air freed from carbon dioxide. The tube *C* and the set of bulbs *DE* are then weighed. The increases in weight in the respective tubes represent the absorbed water and carbon dioxide.

The simultaneous determination of carbon or carbon dioxide and moisture has been discussed on pages 631-5. Assuming that the hygroscopic moisture has been expelled by drying the sample at 110°, a certain proportion of the remaining water in carbonaceous clays will be derived from the clay and the remainder from the organic matter. In such cases, digest a weighed portion of the sample with a mixture of two volumes of fuming hydrofluoric acid and one volume of hydrochloric acid (sp. gr. 1·18); evaporate to dryness. Repeat the

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[1] Freed from carbon dioxide by heating in a porcelain tube.

[2] For the amount of moisture which calcium chloride, sulphuric acid and phosphoric oxide leave in a gas, see page 100.

[3] E. Ludwig, *Tschermak's Mitt.*, (1), **2**, 214, 1875; *Zeit. anal. Chem.*, **17**, 206, 1878; L. Sipöcz, *ib.*, **17**, 207, 1878; *Sitzber. K.K. Akad. Wiss. Wien*, **86**, 51, 1877. The former used a platinum tube; the latter, a platinum boat.

operation three times. Digest the residue with hot water, filter through an asbestos-packed Gooch crucible or carbon tube, wash and dry at 110°. After weighing, the carbon may be detached from the filter and the ratio of carbon to hydrogen determined by combustion of the organic matter to carbon dioxide and water.[1] Jannasch's process or one of the methods indicated in the preceding chapter may be used for the combustion.

EXAMPLE.—A carbonaceous clay gave the following percentage results:—

Jannasch's process .	. Total water	. 14·21
Lissner's process .	. Total organic matter . . .	. 4·32
Combustion process .	. Carbon (calculated from CO_2) .	. 4·16
	Hydrogen (calculated from H_2O) .	. 0·10
	Organic Matter . . .	. 4·26

Hence, 4·26[2] grms. of organic matter have 4·16 grms. of carbon, and 0·10 grm. of hydrogen. But 0·10 grm. of hydrogen corresponds with 0·90 grm. of water. Hence, the sample of clay contained:

Water	. 13·31 per cent.
Organic matter	. 4·32 per cent.

These numbers can only be regarded as an approximate representation of what they are supposed to designate.

According to Danne,[3] the amount of moisture can be determined in many substances by heating them with calcium carbide and measuring the volume of acetylene obtained. The method has been extended to the determination of the "water of crystallisation" in many salts. The method has also been modified by allowing the acetylene to escape and estimating the water from the loss in weight of the apparatus owing to the escape of acetylene.

§ 314. Lindner's Process.

Lindner[4] has shown that water can be determined volumetrically by interaction with α-naphthyldichlorophosphine oxide, $C_{10}H_7.POCl_2$, whereby one molecule of hydrogen chloride is evolved for every molecule of water which reacts. Dittler and Hueber[5] have applied this method to the determination of small quantities of water and of carbon dioxide in silicates. They state that in the analysis of micas and epidotes the process is capable of much

[1] A. Lissner, *Chem. Ztg.*, **34**, 37, 1910. See page 585.

[2] The difference between 4·32 and 4·26 represents analytical errors, or oxygen and nitrogen.

[3] H. A. Danne, *Proc. Soc. Chem. Ind. Victoria*, 1900; P. V. Dupré, *Analyst*, **30**, 266, 1905; **31**, 213, 1906; R. A. Cripps and J. A. Brown, *ib.*, **34**, 519, 1909; I. Masson, *Journ. Chem. Soc.*, **97**, 851, 1910; *Chem. News*, **103**, 37, 1911; A. C. D. Rivett, *ib.*, **104**, 261, 1911; H. C. McNeil, *Chem. Eng.*, **16**, 38, 1912; W. D. Haigh, *Sci. Proc. Roy. Dublin Soc.*, (2), **14**, 529, 1915; R. W. Roberts and A. Frazer, *Journ. Soc. Chem. Ind.*, **29**, 197, 1910; E. A. Fisher and J. Thomlinson, *ib.*, **51**, 355T, 1932; F. H. Campbell, *ib.*, **32**, 67, 1913; H. C. Freeman, Brit. Pat. 335,308, 1929; S. Stanworth, *Trans. Cer. Soc.*, **32**, 443, 1933; W. Franke, *Braun-kohlenarch.*, **36**, 39, 1932; *Chem. Zentr.*, (2), 2770, 1932; I. C. Allen and W. A. Jacobs, *Eighth Inter. Cong. App. Chem.*, **8**, x, 17, 1912. For the use of calcium hydride, see O. Note-varp, *Zeit. anal. Chem.*, **80**, 21, 1930; C. K. Rosenbaum and J. H. Walton, *Journ. Amer. Chem. Soc.*, **52**, 3568, 1930. For Grignard's reagent, see A. Taubmann, *Zeit. anal. Chem.*, **74**, 161, 1928; T. Zerewitinoff, *ib.*, **50**, 680, 1911.

[4] J. Lindner, *Zeit. anal. Chem.*, **66**, 305, 1925; **86**, 141, 1931.

[5] E. Dittler and H. Hueber, *Zeit. anorg. Chem.*, **195**, 41, 1931; **199**, 17, 1931. R. P. Bell (*Journ. Chem. Soc.*, 2903, 1932) states that the isomeric substance, α-naphthoxydichloro-phosphine, $C_{10}H_7O.PCl_2$, dissolved in a neutral solvent, such as benzene or phenyl bromide, reacts much more readily with water vapour than does α-naphthyldichlorophosphine oxide.

greater precision than the usual gravimetric methods, but that its application is limited to substances of low water content.

The experimental details are as follows:—A weighed quantity (0·1–0·2 grm.) of the mineral is heated with powdered quartz and the evolved gases are passed into α-naphthyldichlorophosphine oxide. The hydrogen chloride, resulting from the hydrolysis

$$C_{10}H_7.POCl_2 + 2H_2O = C_{10}H_7.PO(OH)_2 + 2HCl$$

together with any carbon dioxide, are absorbed in a measured excess of 0·01N-barium hydroxide. The excess of barium hydroxide is titrated with 0·01N-hydrochloric acid, using phenolphthalein as indicator. The difference between the volume of the barium hydroxide solution taken and that unused is equivalent to the sum of the evolved hydrogen chloride and carbon dioxide. To determine the carbon dioxide, the neutralised solution is boiled with a known excess of standard hydrochloric acid until the precipitated barium carbonate has been decomposed and all the carbon dioxide expelled from the solution. The excess of acid is then determined by titration with standard barium hydroxide.

§ 315. Fractional Dehydration : Water Lost at Different Temperatures.

Some zeolites and hydrated alumino-silicates give off water [1] below 110°, and in that case the silicate can be heated at, say, 100°, 110°, 120°, 130°, . . .
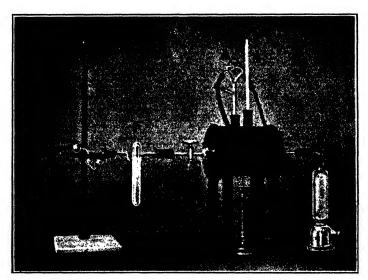
FIG. 136.—Fractional Dehydration.

to find if the substance loses appreciable amounts of water at progressively higher temperatures. The results are then represented as "water below 100°," "water between 100° and 110°," etc. When the water is to be determined at different temperatures in this way, a double walled copper cylinder is fitted up, as shown in fig. 136, with a thermo-regulator, A, and thermometer, B.

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[1] For the gases in silicates, see A. P. Lidoff, *Zeit. anal. Chem.*, 46, 357, 1907; R. T. Chamberlain, *The Gases in Rocks*, Washington, 1908.

A glass tube, say 30 cm. long and 3·5 or 4 cm. wide, is closed at one end by a hollow ground glass stopper which is fused to a stopcock C. The other end of the glass tube is drawn out and connected to a drying tower, E.

The copper cylinder has an outer jacket of asbestos. The glass tube is plugged in the copper tube with carded asbestos. By adjusting the thermo-regulator, any material, placed in a small squat uncovered weighing bottle, resting in the glass tube, can be heated in the furnace to any desired tempera-ture for any length of time while a current of air is drawn through the apparatus. The air is dried by passing it through a drying tower, E. This tube is packed with soda lime and calcium chloride, the former to remove carbon dioxide, the latter, moisture. A weighed calcium chloride tube, F, is placed at the end C to absorb any moisture driven from the substance in the weighing bottle. The increase in weight of this tube during an experiment represents the moisture driven from the substance. The result may also be checked by finding the loss of weight of the weighing bottle. The two may not necessarily coincide, since volatile substances other than water may be driven off. The small bulbs g contain sulphuric acid. These show the rate at which air is passing through the apparatus, by counting the number of bubbles per second.[1]

If the cock C be closed, and the other end connected with a suction pump, the substance can be heated under reduced pressure. In that case, the tube F is fitted to the opposite end of the glass tube.

Guttmann's[2] weighing bottle, fig. 137, is useful for heating substances to a constant weight in a current of gas, and hence determining the loss in weight on heating to different temperatures. The gas entry and exit tubes have ground caps for protecting the contents from air during the weighing.

Meyer's[3] vapour bath or oil bath is useful when a small amount of a substance is to be heated to a given temperature below about 200°. The bath

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[1] J. W. Mellor (*Trans. Cer. Soc.*, 7, 114, 1908) describes a method for heating the tube electrically at any desired temperature. If the joints of the furnace in the preceding diagram be brazed, and the thermo-regulator, A, replaced by a reflux condenser, liquids of known boiling-points can be used. For instance:

Table LIX.—Liquids for Vapour-Baths.
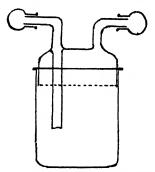
Liquid.	Temperature available.
Benzene	80–81°
Water	99–100°
Toluene	109–112°
Ethyl n-butyrate	120–121°
Amyl alcohol	128–132°
Xylene	139–141°
Cumene	152–153°
Pseudocumene	165–168°
p-Cymene	175–177°
Aniline	180–184°
Dimethylaniline	191–193°
Nitrobenzene	209–210°

The temperature of the inner chamber is generally 2° to 5° lower than the boiling-point of the liquid in the outer chamber.

[2] L. F. Guttmann, *Journ. Amer. Chem. Soc.*, 28, 1667, 1906.

[3] V. Meyer, *Ber.*, 18, 2999, 1885; A. Fock, *ib.*, 18, 1124, 1885.

is shown in section in fig. 138. A porcelain cylinder is placed inside a double-walled copper cylinder. The crucible containing the substance under investigation is placed in the inner cylinder. A suitable liquid is placed in the copper vessel. The latter is fitted with a condenser, C. A small flame and a
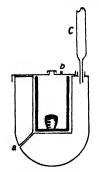
FIG. 137.—Guttmann's Weighing Bottle. FIG. 138.—Meyer's Vapour Bath.

small amount of liquid are needed for the work. For temperatures higher than 200°, oils may be used. A current of air circulates outside the inner cylinder, entering at a and leaving at b.

It seems fairly certain that some clays lose more moisture when dried under reduced pressure over sulphuric acid [1] than when they are heated to constant weight in the hot oven, fig. 58, page 134. Skertchly [2] has shown that many organic substances behave similarly.

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[1] E. Löwenstein, *Zeit. anorg. Chem.*, **63**, 69, 1909.
[2] W. P. Skertchly, *Journ. Soc. Chem. Ind.*, **32**, 70, 1913. Compare T. F. Winmill, *Trans. Inst. Min. Eng.*, **51**, 484, 1916.

CHAPTER XL.

THE DETERMINATION OF BORON.

§ 316. The Detection of Boric Oxide.

THE following remarks on this subject supplement those given in the regular text-books on qualitative analysis. It is generally necessary to get the borate in a soluble condition. This is done by fusing the borosilicate with five to ten times its weight of sodium carbonate and extracting the cold mass with water.

The Alcohol Flame Test.—Boric acid dissolves in alcohol and the solution burns with a flame tinged with green. Similarly, if a borate be decomposed by treatment with an acid [1] and the mass be mixed with alcohol, the alcohol, when ignited, burns with a greenish flame. The test is carried out by igniting the mixture on a watch-glass.[2] It is possible to detect 0·001 per cent. of boric oxide in a solution by the flame test, and a glaze containing 0·1 per cent. of boric oxide will give a distinct reaction.

If copper be present, the test is not satisfactory. The copper must be first removed by hydrogen sulphide. Barium salts also colour the flame green. If sulphuric acid be used to decompose the borate, non-volatile barium sulphate is formed and barium does not then interfere with the test. When copper or barium is present, the flame test is best made by placing the mixture in a six-inch test tube fitted with a cork and gas-jet as illustrated in fig. 139. The test tube is heated and, when the alcohol begins to boil, the issuing vapours are lighted with a second burner. The copper and barium do not then interfere. If metallic chlorides be present, ethyl chloride may be formed and this colours the flame green, thus spoiling the test. This difficulty is easily avoided by using sulphuric or nitric acid, not hydrochloric acid.

The Glycerol Flame Test.[3]—The powdered and calcined borate is moistened with sulphuric acid and heated on platinum foil until the acid is expelled. Moisten the mass with glycerol and light. The glycerol burns with a green flame if boric oxide be present. The glycerol test will indicate 0·001 per cent. of boric oxide. For the disturbing agents, see the alcohol flame test.

Turmeric Test.—If a borate be just acidified with dilute hydrochloric acid, and a strip of turmeric paper [4] be half immersed in the solution, no apparent

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[1] The borate is supposed to be decomposable by treatment with acids—sulphuric, hydrochloric or hydrofluoric acid; or by a mixture of ammonium nitrate and chloride; sulphuric and hydrochloric acids; or sulphuric and nitric acids. If methyl alcohol be used, the acid treatment is unnecessary, even with borax—E. Pieszezek, *Pharm. Centr.*, 83, 362, 1913.

[2] H. Bornträger, *Zeit. anal. Chem.*, 39, 92, 1900; M. Bidaud, *Compt. rend.*, 76, 489, 1873; 80, 387, 1875; M. Dieulafait, *ib.*, 85, 605, 1877; *Ann. Chim. Phys.*, (5), 12, 318, 1877; A. Gabriel and H. G. Tanner, *Journ. Amer. Chem. Soc.*, 50, 1385, 1928; W. Stahl, *Latvij Univ. Raksti*, 1, 369, 401, 1930; *Zeit. anal. Chem.*, 83, 340, 1931.

[3] M. W. Iles, *Amer. Chem.*, 6, 361, 1876; H. Gilm, *Ber.*, 11, 712, 1878.

[4] Turmeric paper gives a brownish colour with alkalies, yellow with acids. E. Schlumberger, *Bull. Soc. chim.*, (2), 5, 194, 1866; P. Kulisch, *Zeit. angew. Chem.*, 7, 147, 1894; H. Jay and

change occurs; but if the paper be dried on a watch-glass at 100°, the half which has been dipped in the boric acid shows a peculiar brownish-red coloration. If but a small trace of boric oxide be present, the stain may be pink.

The colour remains when the stain is dipped in boric acid again, or in dilute sulphuric or hydrochloric acid. The brown stain produced by alkalies changes into yellow under these conditions. If too little acid be used, there may be no coloration; if too much, the colour may be brown. If the boric acid stain be touched with a solution of potassium hydroxide, the paper becomes bluish-black or bluish-grey, according as much or little boric acid be present. A little hydrochloric acid will restore the red colour. As little as 0·0001 grm. of boric acid can be detected by the (pink) colour produced in this way. Oxidising agents like chlorates and chromates interfere with the test by destroying the turmeric. Nitric acid is an exception. Iodides[1] also interfere. Concentrated hydrochloric acid may give a dark brown stain under the conditions of the test; ferric chloride, molyb-

FIG. 139.—Flame Test for Boric Oxide.

denum and zirconium salts give a brownish-red stain which is not coloured bluish-black with potash solution.

Still smaller amounts of boric oxide can be detected if needed by placing the solution under investigation in a small porcelain dish and evaporating it to dryness in a desiccator *in vacuo* at a low temperature. If a few drops of an alcoholic extract of a few turmeric papers be mixed in the dish with the borate, the solution acidified with acetic acid and evaporated to dryness on a water bath, a reddish-brown residue will be obtained if as little as 0·0002 grm. of B_2O_3 be present, while 0·00002 grm. will produce a perceptible coloration.[2]

M. Dupasquier, *Monit. Scient.*, 9, 709, 1895; G. Bertrand and H. Agulhon, *Ann. Chim. anal.*, 15, 45, 1910; *Bull. Soc. chim.*, (4), 7, 90, 1910; *Compt. rend.*, 157, 1433, 1913; 158, 201, 1914; H. Fonzes-Diacon and R. Fabre, *ib.*, 158, 1541, 1914; N. Camus, *Anal. Soc. Quim. Argentina*, 2, 123, 1914; H. Hawley, *Analyst*, 40, 150, 1915; E. M. Chamot and H. I. Cole, *Journ. Ind. Eng. Chem.*, 10, 48, 1918; W. W. Scott and S. K. Webb, *ib.*, *Anal. Ed.*, 4, 180, 1932; N. A. Tananaev and O. A. Kul's'ka, *Ukrain Khem. Zhur.*, 9, *Wiss.-tech., Teil*, 1–15, 1934.

[1] Chlorates and chromates may be reduced by treating the solution with solid sodium sulphite; add hydrochloric acid and warm the solution to drive off the excess of sulphurous acid. Filter, if necessary, and boil the filtrate with a slight excess of sodium carbonate, dilute and filter. Iodides, if present, may be removed by precipitation with silver nitrate in a solution acidified with nitric acid. The addition of 5 grms. of urea per 100 c.c. of solution inhibits the effects of nitrites; nitrates do not interfere—T. M. Price and E. H. Ingersoll, *Bull. U.S. Dept. Agric. (Chem.)*, 137, 115, 1912.

[2] M. Ripper, *Weinbau Weinhandl.*, 6, 331, 1888; P. Kulisch, *Zeit. angew. Chem.*, 7, 187, 1894; V. Lenher and J. S. C. Wells, *Journ. Amer. Chem. Soc.*, 21, 417, 1899; H. Bornträger, *Zeit. anal. Chem.*, 39, 92, 1900; W. H. Low, *Journ. Amer. Chem. Soc.*, 28, 807, 1906; E. Schlumberger, *Bull. Soc. chim.*, (2), 5, 194, 1866; L. Robin, *ib.*, (4), 13, 602, 1913; G. Bertrand and H. Agulhon, *Compt. rend.*, 157, 1433, 1913.

The Boron Fluoride Test.—If the powdered borate be mixed with a few drops of water and approximately three times its weight of Turner's flux [1] and the paste be exposed on the loop of a platinum wire in the outer mantle of a Bunsen flame, the boron fluoride which is formed imparts a greenish tinge to the flame. The reaction will detect 0·01 per cent. of B_2O_3 in a silicate.[2]

§ 317. The Determination of Boric Oxide.

In 1851, Rose [3] stated that the quantitative determination of boric oxide was so very difficult that up to that time no method had been devised which gave a direct result.[4] The problem has since been solved, but the process is difficult and laborious. Rosenbladt [5] thinks this "one of the most complicated operations in analytical chemistry." Vogt [6] estimated the boric oxide in silicates by difference after the other constituents had been determined. This method is not recommended. Several indirect methods have been proposed.[7] The isolation of a definite compound of boric oxide from the associated constituents is a necessary preliminary for the successful determination of boric oxide. The removal of silica and alumina is particularly difficult. Ferric oxide and alumina, for instance, when precipitated by ammonia carry down some boric oxide.[8] The silica also is difficult to separate without loss of boric oxide, because, if the mixture be treated with hydrofluoric and sulphuric acids in the usual way, boron is volatilised as boron fluoride. Conversely, if the acid treatment for the removal of silica be omitted, silica may contaminate the compound of boron which is finally weighed.[9] Before dealing with complex silicates, it will be convenient to take simpler problems; and first, the volumetric determination of boric oxide in boric acid.

Volatilisation of Boric Oxide and Borax.—At the outset it is necessary to emphasise the fact that the substances now under investigation are somewhat volatile. For example, there is a difficulty in drying boric acid, since a comparatively large amount of boric oxide is lost. For instance, the loss of

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[1] TURNER'S FLUX.—Mix finely powdered calcium fluoride or potassium fluoride with 4·5 times its weight of potassium bisulphate. Hydrofluosilicic acid may be used in place of this flux if the borate is easily decomposed—E. Turner, *Edin. Phil. Journ.*, **14**, 124, 1826; *Pogg. Ann.*, **6**, 489, 1826. When a substance containing a borate is mixed with this flux, it is supposed that fluoboric acid is formed which, being volatile, imparts a momentary green coloration to the edge of a flame. Three to four parts of the flux are taken to one of the substance under test. The test fails with sodium borate and succeeds with most other borates and borosilicates, but these give a green flame, without Turner's flux, *per se* equally well—H. How, *Chem. News*, **18**, 203, 1868; *ib.*, **20**, 241, 1869; E. J. Chapman, *Phil. Mag.*, (5), **2**, 459, 1876; K. Buzengeiger, *Ann. de Chim.*, (2), **41**, 205, 1829. J. J. Berzelius also pointed out that axinite gives a green coloration *per se*.

[2] E. J. Chapman, *Chem. News*, **35**, 12, 26, 36, 1877; C. le Neve Foster, *ib.*, **35**, 127, 1877; H. Kämmerer, *Zeit. anal. Chem.*, **12**, 376, 1873. For the spectrographic detection of boron, see A. de Grammont, *Compt. rend.*, **166**, 477, 1918; W. C. Holmes, *Journ. Assoc. Off. Agric. Chem.*, **10**, 522, 1927; J. S. McHargue and R. K. Calfee, *Ind. Eng. Chem. Anal. Ed.*, **4**, 385, 1932.

[3] H. Rose, *Ausführliches Handbuch der analytischen Chemie*, Braunschweig, **2**, 721, 1851.

[4] G. S. Smith (*Analyst*, **60**, 735, 1935) has devised a colorimetric process for the determination of boric oxide by means of quinalizarin.

[5] T. Rosenbladt, *Zeit. anal. Chem.*, **26**, 18, 1887.

[6] G. Vogt, *Ber. Internat. Kongress angew. Chem.*, **5**, i, 738, 1904; H. Rose, *l.c.*

[7] A. Arfvedson, *Schweigger's Journ.*, (2), **8**, 1, 1802; F. G. Schaffgotsch, *Pogg. Ann.*, **107**, 427, 1859; J. J. Berzelius, *ib.*, **2**, 118, 1824; H. Rose, *ib.*, **80**, 261, 1850; K. Kraut, *Zeit. anal. Chem.*, **1**, 73, 1862.

[8] F. Wöhler, *Liebig's Ann.*, **141**, 268, 1867.

[9] *E.g.* in A. Stromeyer's process (*Liebig's Ann.*, **100**, 82, 1856) every one part by weight of silica contaminating the final precipitate quadruples the calculated amount of boric oxide.

boric oxide on driving off the water of hydration from 1 grm. of boric acid was as follows[1]:—

Water	.	0·7808	0·7543	0·7492	0·7544	0·2885	0·2780	0·2783 grm.
B_2O_3 lost	.	0·1405	0·1358	0·1449	0·1508	0·0896	0·1034	0·1032 grm.

Aqueous solutions containing boric acid, or solutions of borax acidified with sulphuric or hydrochloric acid, lose much boric acid when evaporated. In illustration, some of Tschijewski's experiments might be quoted—

B_2O_3 present	.	0·6030	0·2638	0·1268	0·0323	0·0314	0·0095 grm.
B_2O_3 lost	.	.	0·0522	0·0298	0·0278	0·0123	0·0114	0·0071 grm.

on evaporation to dryness on a water bath.[2]

Borax also during calcination loses boric oxide. Thus, Waldbott[3] found that when 0·6532 grm. of borax glass was blasted:—

Time .	.	5	12	22	29	39	44	46 minutes.
Loss .	.	0·8	1·0	2·0	2·5	3·3	4·1	4·2 per cent.

Starting with 2·1320 grms., 10 minutes' calcination over an ordinary Bunsen burner gave no loss; 15 minutes over a moderate blast, with the crucible half covered, gave a loss of 0·0014 grm.; and over a strong blast, with the crucible open, 0·0073 grm. was lost. In a pottery oven, fired to Seger's cone 9 (scheduled 1280°):—

Time	.	.	.	60	48	26	3 hours.
Loss	.	.	.	48·98	22·40	7·88	1·47 per cent.

Hence boric oxide may also be lost when the "loss on ignition" is determined.

§ 318. The Evaluation of Boric Acid.

An aqueous solution of boric acid can be titrated with a standard solution of sodium hydroxide. Unfortunately, owing to the feeble acidic properties of this acid, the pink colour of the indicator, phenolphthalein, is developed before all the boric acid is neutralised. If, however, the solution contains sufficient glycerol or mannitol,[4] the boric acid all reacts with the sodium hydroxide to form sodium metaborate—

$$NaOH + H_3BO_3 = 2H_2O + NaBO_2$$

[1] P. Tschijewski, Arch. Sci. phys. nat., (3), 12, 120, 1884; Bull. Soc. chim., (2), 42, 324, 1884; H. Lescœur, Ann. Chim. Phys., (6), 19, 43, 1890; L. Kahlenberg and O. Schreiner, Zeit. phys. Chem., 20, 547, 1896; F. W. Skirrow, ib., 37, 84, 1901; R. Bunsen, Liebig's Ann., 111, 257, 1859; O. Hehner, Analyst, 16, 141, 1891.

[2] L. de Koningh, Journ. Amer. Chem. Soc., 19, 385, 1897; F. G. Schaffgotsch, Pogg. Ann., 107, 427, 1859; J. A. Rose, Beiträge zur Kenntnis der Borsäure und über eine direkt gewichts-analytische Bestimmung derselben, Bonn a. Rh. (Erlangen), 1902; F. W. Skirrow, Zeit. phys. Chem., 37, 84, 1901.

[3] S. Waldbott, Journ. Amer. Chem. Soc., 16, 410, 1894; E. Cramer, Tonind. Ztg., 16, 155, 1892. See page 664.

[4] D. Klein, Bull. Soc. chim., (2), 29, 178, 195, 1878; Compt. rend., 86, 826, 1878; 99, 144, 1884; M. Copaux, ib., 127, 756, 1898; A. Lambert, ib., 108, 1016, 1889; A. Senier and A. J. G. Lowe, Pharm. Journ., (3), 8, 819, 1878; W. R. Dunstan, ib., (3), 14, 41, 1884; R. Sulzer, Deut.-Amer. Apoth. Ztg., 596, 1886; K. Jehn, Arch. Pharm., (3), 25, 250, 1887; (3), 26, 495, 1888; E. Donath, Chem. Ztg., 17, 1826, 1893; E. H. Farrington, Rev. Internat. Falsif., 10, 81, 1897; G. Denigès, Journ. Pharm. Chim., (6), 6, 49, 1897; V. Gasselin, Ann. Chim. Phys., (7), 3, 1, 1884; C. Schwarz, Pharm. Ztg., 32, 562, 1894; N. Tananaeff and D. Tsukerman, Journ. Russ. Phys. Chem. Soc., 41, 1469, 1909; E. Salm, Zeit. phys. Chem., 57, 471, 1906; E. Salm and H. Friederthal, Zeit. Elektrochem., 13, 128, 1907; C. L. A. Schmidt and C. P. Finger, Journ. Phys. Chem., 12, 413, 1908; N. Dhar, Zeit. anorg. Chem., 86, 196, 1914.

before the pink of phenolphthalein appears. The polyhydric alcohol augments,[1] so to speak, the acidic qualities of the acid in question, probably owing to the formation of a complex.

Thomson [2] has a process for the volumetric determination of boric acid based on these phenomena. Dissolve, say, 7·5 grms. of the boric acid in about 350 c.c. of water in a 500 c.c. flask, and make the solution up to the 500 c.c. mark with water. Pipette 50 c.c. into an Erlenmeyer's flask; add 50 c.c. of glycerol,[3] or a gram of mannitol,[4] and titrate with approximately 0·5N-sodium hydroxide solution free from carbonates,[5] using phenolphthalein as indicator.[6]

[1] K. Farnsteiner, *Zeit. Untersuch. Nahr. Genuss.*, 5, 1, 1902; A. Beythein and H. Hempel, *ib.*, 2, 842, 1899; B. Fischer, *ib.*, 3, 17, 1900; G. Magnanini, *R. Accad. Lincei*, 6, 260, 411, 1890; *Gazz. Chim. Ital.*, 20, 441, 448, 1890; 21, ii, 134, 1891; *Zeit. phys. Chem.*, 6, 58, 1890; L. Kahlenberg and O. Schreiner, *ib.*, 20, 547, 1896; W. Vaubel and E. Bertlet, *Chem. Ztg.*, 29, 629, 1905; A. Wogrinz and J. Kittel, *Chem. Ztg.*, 36, 433, 1912; J. J. Fox and A. G. H. Gauge, *Journ. Chem. Soc.*, 99, 1075, 1911.

[2] R. T. Thomson, *Journ. Soc. Chem. Ind.*, 12, 432, 1893; *Analyst*, 21, 64, 1896; A. H. Allen and A. R. Tankard, *ib.*, 29, 301, 1904; F. W. Richardson and W. K. Walton, *ib.*, 38, 140, 1913; A. S. Dodd, *ib.*, 54, 645, 715, 1929; 55, 23, 1930; M. Barthe, *Journ. Pharm. Chim.*, (5), 29, 163, 1894; M. Vadam, *ib.*, (6), 8, 109, 1898; M. Hönig and G. Spitz, *Zeit. angew. Chem.*, 9, 549, 1896; G. Jorgensen, *ib.*, 10, 5, 1897; N. Tananaeff and D. Tsukerman, *Journ. Russ. Phys. Chem. Soc.*, 41, 1469, 1909; P. Nicolardot and J. Boudet, *Bull. Soc. chim.*, (4), 21, 97, 1917; J. Prescher, *Zeit. Nahr. Genussm.*, 36, 283, 1918; P. Jannasch and F. Noll, *Journ. prakt. Chem.*, (2), 99, 1, 1919; H. Rath, *Naturprodukte*, 134, 1923; L. A. Congdon and J. M. Rosso, *Chem. News*, 129, 219, 1924; M. Cikrtová and K. Sandera, *Chem. Listy*, 19, 179, 1925; R. Schmidt, *Sprechsaal*, 59, 541, 1926; *Chem. Zentr.*, (2), 2010, 1926; G. Vastagh, *Magyar Chem. Fol.*, 37, 55, 1931; E. Schulek and G. Vastagh, *Zeit. anal. Chem.*, 84, 167, 1931; F. J. Foote, *Ind. Eng. Chem. Anal. Ed.*, 4, 39, 1932; D. J. Pflaum and H. H. Wenzke, *ib.*, 4, 392, 1932; J. C. Krantz and C. J. Carr, *Journ. Amer. Pharm. Assoc.*, 21, 350, 1932; F. L. Hahn, R. Klockmann and R. Schultz, *Zeit. anorg. allgem. Chem.*, 208, 213, 1932; E. Vincke, *Chem. Ztg.*, 57, 695, 1933; R. S. Ashel'rod and M. L. Erukhimova, *Zavodskaya Lab.*, 3, 121, 1934.

[3] GLYCEROL SOLUTION.—Glycerol 10, water 1, by volume. The glycerol must be free from fatty acids or the fatty acids must be neutralised just before use with 0·1N-sodium hydroxide solution. Glycerol usually becomes acid on keeping, possibly owing to the slow decomposition of fatty impurities. For the solubility of boric acid in aqueous glycerol, see W. Herz and M. Knoch, *Zeit. anorg. Chem.*, 45, 262, 1905; P. Mueller and R. Abegg, *Zeit. phys. Chem.*, 57, 514, 1906.

[4] MANNITOL (M. Vadam, *Chem. News*, 78, 271, 1898; L. C. Jones, *Amer. J. Science*, (4), 7, 127, 1899; *Chem. News*, 80, 65, 1899; A. Grün and H. Nossovitsch, *Monats.*, 37, 409, 1916; A. S. Dodd, *Analyst*, 55, 23, 1930; G. Vastagh, *Magyar Chem. Fol.*, 37, 55, 1931; E. Schulek and G. Vastagh, *Zeit. anal. Chem.*, 84, 167, 1931; F. J. Foote, *Ind. Eng. Chem. Anal. Ed.*, 4, 39, 1932; D. J. Pflaum and H. H. Wenzke, *ib.*, 4, 392, 1932) is more convenient than glycerol. It is solid, easily handled, does not alter the bulk of the solution and is not so liable to contamination with acids. The end-point is also a little sharper. The results are quite as accurate as with glycerol. The choice is therefore a matter of convenience. L. E. Iles (*Analyst*, 43, 323, 1918) recommends manna; G. van B. Gilmour (*ib.*, 49, 576, 1924), invert sugar; L. S. Weatherby and H. H. Chesney (*Ind. Eng. Chem.*, 18, 820, 1926), glucose.

[5] Carbonates interfere with the indicator and react: $2B_2O_3 + Na_2CO_3 = Na_2B_4O_7 + CO_2$. Hence, a little barium hydroxide is sometimes added during the preparation of the sodium hydroxide solution. See discussion, page 52. F. P. Venable and J. S. Callison (*Chem. Ztg.*, 14, 167, 1890) report as much as 0·06 per cent. of boric oxide in caustic soda and caustic potash sold as "pure." M. Gorges, *Journ. Pharm. Chim.*, (6), 3, 346, 1896; P. Jannasch and F. Noll (*Journ. prakt. Chem.*, (2), 99, 1, 1919) titrate with alcoholic sodium ethoxide solution and thus eliminate the interference of carbon dioxide.

[6] Other indicators have been recommended: litmus (J. L. Gay-Lussac, *Ann. Chim. Phys.*, (2), 40, 398, 1830. See F. Fichter, *Journ. Chim. phys.*, 13, 399, 1915); lacmoid (R. T. Thomson, *Chem. News*, 47, 123, 135, 1883); congo red (C. Schwarz, *Pharm. Ztg.*, 37, 562, 1887); helianthine (F. Parmentier, *Compt. rend.*, 113, 41, 1891); orceine (M. de Luynes, *Ann. Chim. Phys.*, (4), 6, 184, 1865); hæmatoxyline (A. Guyard, *Bull. Soc. chim.*, (2), 40, 422, 1883); Porrier's blue (R. Engel, *ib.*, (2), 45, 327, 1886; *Compt. rend.*, 102, 214, 262, 1886); tincture of red rose leaves (M. Barthe, *Journ. Pharm. Chim.*, (5), 29, 163, 1894); tincture of mimosa blossoms (L. Robin, *Ber. Internat. Cong. App. Chem.*, 8, i, 429, 1912).

When the pink colour appears, add 10 c.c. of glycerol, or another gram of mannitol. If the pink colour disappears, continue the titration with the sodium hydroxide. Repeat the addition of glycerol or mannitol and titration until the pink colour persists when more mannitol or glycerol is added.

EXAMPLE.—23·7 c.c. of a 0·5N-solution of sodium hydroxide were required for a titration. This solution contains 20·00 grms. of NaOH per litre, which, according to the equation: $NaOH + H_3BO_3 = 2H_2O + NaBO_2$, corresponds with 30·92 grms. of H_3BO_3 per litre, or 1 c.c. of the standard solution is equivalent to 0·03092 grm. of H_3BO_3. Hence, $23·7 \times 0·03092 = 0·7328$ grms. of H_3BO_3 per 50 c.c.; or 14·656 grms. per 1000 c.c.; or per 15 grms. of the sample. Hence, the sample has 97·7 per cent. H_3BO_3.

According to Prideaux,[1] tropæolin O (sodium p-benzeneazoresorcinol sulphonate—0·5 c.c. of a 0·04 per cent. solution for a total volume of about 68 c.c.) is the best indicator to use since titrations can be made accurate to ± 1 per cent. in dilute or concentrated solutions, with or without the addition of sodium chloride and possibly with or without the addition of glycerol or mannitol.

Will and Zschimmer [2] titrate the boric acid with baryta water; Smith [3] adds standard manganese sulphate and titrates with standard potassium permanganate; and Jones [4] liberated iodine from a mixture of potassium iodide and iodate in presence of boric acid and mannitol, and determined the iodine by titration with sodium thiosulphate.[5]

§ 319. The Evaluation of Borax.

Solutions containing boric acid are neutral to p-nitrophenol and to methyl orange, but acid towards phenolphthalein—particularly in the presence of mannitol or glycerol. Hence, if hydrochloric acid be added to an aqueous solution of borax, using p-nitrophenol or methyl orange as indicator,[6] the solution will react acid only when all the boric acid is free and all the soda is neutralised by the hydrochloric acid. The reaction is represented:

$$Na_2B_4O_7 + 5H_2O + 2HCl = 2NaCl + 4H_3BO_3$$

The boric acid can then be titrated as just indicated above. The determination is made in the following way:—

[1] E. B. R. Prideaux, *Zeit. anorg. Chem.*, **83**, 362, 1913.

[2] H. Will, *Arch. Pharm.*, **225**, 1101, 1887; R. Hefemann, *Pharm. Centr.*, (2), **9**, 116, 1888; E. Zschimmer, *Chem. Ztg.*, **25**, 44, 67, 1901.

[3] E. F. Smith, *Amer. Chem. Journ.*, **4**, 279, 1883; *Chem. News*, **46**, 286, 1882; J. Volhard, *Liebig's Ann.*, **98**, 318, 1879; C. Bodewig, *Zeit. anal. Chem.*, **23**, 143, 1884; G. Carinelli, *Gazz. Chim. Ital.*, **31**, i, 544, 1901.

[4] L. C. Jones, *Zeit. anorg. Chem.*, **20**, 212, 1899; **21**, 169, 1899; A. Stock, *Compt. rend.*, **130**, 516, 1900; M. Barthe, *Journ. Pharm. Chim.*, (5), **29**, 163, 1894; J. Prescher, *Arch. Pharm.*, **242**, 194, 1904; P. Georgevič, *Journ. prakt. Chem.*, (2), **38**, 118, 1888.

[5] For the electrometric titration of boric acid, see J. A. M. van Liempt, *Rec. Trav. chim.*, **39**, 358, 1920; *Zeit. anorg. Chem.*, **111**, 151, 1920; M. G. Mellon and V. N. Morris, *Proc. Indiana Acad. Sci.*, **35**, 85, 1924; M. G. Mellon and F. R. Swan, *Ind. Eng. Chem.*, **19**, 1354, 1927; L. V. Wilcox, *ib.*, *Anal. Ed.*, **4**, 38, 1932; I. V. Grebenschtschikov and T. A. Favorskaia, *Journ. Russ. Phys. Chem. Soc.*, **61**, 561, 1929. In the presence of phosphoric acid, I. M. Kolthoff (*Chem. Weekb.*, **19**, 449, 545, 1922; B. Pfyl, *Arb. Kais. Gesund. Amt.*, **47**, 1, 1914) adds sodium citrate, which prevents the interference of boric acid during the titration of the phosphoric acid with sodium hydroxide. In the neutralised solution, the boric acid is titrated as indicated above. Compare, however, W. W. Deerns, *Chem. Weekb.*, **19**, 480, 1922; **25**, 268, 1928.

[6] R. T. Thomson (*Chem. News*, **47**, 135, 1883), after comparing litmus, methyl orange, phenolacetolin and phenolphthalein, says: "Methyl orange is by far the best indicator for the estimation of soda in borax, and is, indeed, perfect in that respect. The change in colour at the end of the experiment is very sharply defined." B. H. St. John (*Amer. Journ. Pharm.*, **89**, 8, 1917) recommends methyl red rather than methyl orange.

Dissolve 10 grms. of borax in about 300 c.c. of distilled water, freed from carbon dioxide by boiling, and make the solution up to 500 c.c. with similarly boiled water. Titrate 100 c.c. with approximately 0·5N-hydrochloric acid, using a drop of p-nitrophenol or methyl orange as indicator. Note the volume of hydrochloric acid needed for the neutralisation of the 100 c.c. pipetted from the main solution. Add the same volume of the solution of hydrochloric acid to another 100 c.c. of the borax solution, add glycerol or mannitol as indicated under boric acid, and titrate, as there described, with, say, 0·5N-sodium hydroxide, using phenolphthalein as indicator.

EXAMPLE.—10 grms. of the sample made up to 500 c.c. Of this, 100 c.c., that is, 2 grms. of the sample, required 21 c.c. of the hydrochloric acid solution, and 45·6 c.c. of the standard sodium hydroxide solution, 1 c.c. of which corresponded with 0·0437 grm. of hydrated borax. Hence, 2 grms. of the sample had $45·6 \times 0·0437 = 1·993$ or 99·6 per cent. of hydrated borax.

A similar procedure is used for anhydrous borax, but the weight of the sample taken should be reduced to about 5 grms. Again, with calcined borax, which dissolves only slowly in water, the weighed sample is shaken in a well-corked flask with excess of cold, freshly boiled distilled water until solution is complete.

The relation between the sodium oxide and the boric oxide in borax is not always that corresponding with $Na_2O . 2B_2O_3$, because some sodium metaborate —$Na_2O . B_2O_3$—may be present. This would lead to high values when the borax is calculated from the amount of B_2O_3, since some should then have been calculated to $NaBO_2 . 4H_2O$.

Jacobi's Process.—Jacobi [1] abbreviates the process by taking advantage of the fact that in the presence of glycerol a solution of borax is acid to phenolphthalein, while a solution of sodium metaborate is neutral. Hence, if a solution of borax containing an excess of glycerol be titrated with 0·5N-sodium hydroxide, we have

$$Na_2B_4O_7 + 2NaOH = 4NaBO_2 + H_2O$$

at the neutral point. After making an allowance for any acid in the glycerol, multiply the results by 0·03482 and the product represents the amount of boric oxide in the weight of the sample taken; if multiplied by 0·05032, the result represents the amount of anhydrous borax; and if multiplied by 0·09536, the amount of hydrated borax.

EXAMPLE.—2 grms. of calcined borax were dissolved in water and mixed with glycerol and phenolphthalein. 39·65 c.c. of 0·5N-NaOH were needed. The glycerol added required 0·4 c.c. of the alkali for neutralisation. Hence, $39·65 - 0·4 = 39·25$ c.c. were needed for the titration. Thus the 2 grms. contained $39·25 \times 0·03482 = 1·3667$ grm. of B_2O_3; that is, $1·3667 \times 50 = 68·3$ per cent. of boric oxide, or 98·8 per cent. of calcined borax.

§ 320. The Evaluation of Borocalcite, Boronatrocalcite, Boracite and Calcium Borate.

Digest, say, 10 grms. of powdered borocalcite in a flask fitted with a reflux condenser [2] (fig. 140) with, say, 50 c.c. of 0·5N-hydrochloric acid in order to

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[1] K. Jacobi, *Journ. Amer. Chem. Soc.*, 26, 91, 1904. M. François and L. Seguin (*Journ. Pharm. Chim.*, 6, 244, 1927) dissolve 1·91 grm. of finely powdered borax in 25 c.c. of water and 50 c.c. of glycerol by heating for 30 minutes on a water bath. They then cool and titrate with 1·0N-NaOH in the presence of phenolphthalein: 1 c.c. of 1·0N-NaOH≡0·191 grm. of $Na_2B_4O_7 . 10H_2O$.

[2] V. Kreussler, *Zeit. anal. Chem.*, 24, 80, 1885; J. Walter, *Dingler's Journ.*, 251, 637, 1884.

remove the carbon dioxide, liberate the boric acid from combination and prevent loss of boric acid by volatilisation in steam during the expulsion of the carbon dioxide. Cool. Wash the condenser tube and the contents of the flask into a 500 c.c. standard flask with cold, freshly boiled, distilled water. The insoluble residue can be filtered off, dried and weighed, if desired. Make the solution up to the 500 c.c. mark with water. Pipette 50 c.c. of this solution into a flask, and titrate with standard sodium hydroxide (say, 0·5N), using p-nitrophenol as indicator. When the yellow colour of the indicator appears,[1] all the hydrochloric acid has been neutralised by the soda. Note the volume of the standard sodium hydroxide required for this purpose. Pipette another 50 c.c. of the solution, add the same amount of sodium hydroxide and then titrate with sodium hydroxide and mannitol or glycerol, with phenolphthalein as indicator, as indicated under borax and boric acid.

EXAMPLE.—The solution from 10 grms. of the borocalcite was made up to 500 c.c. and 50 c.c. (*i.e.* 1 grm. of the sample) were taken for the titration. 26·6 c.c. of the soda solution were used in the second titration. 1 c.c. of 0·5N-sodium hydroxide corresponds with 0·01741 grm. of boric oxide, B_2O_3. Hence, $26·6 \times 0·01741 = 0·4631$ grm., or 46·31 per cent. B_2O_3 in the given sample.

Schaak's Process.- If appreciable quantities of iron and alumina be present, both should be separated, if possible, before the titration, since
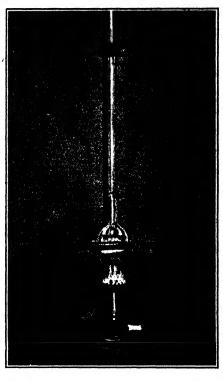
FIG. 140.—Reflux Condenser (see page 306).

alumina will combine with the alkalies as the solution approaches the neutral point and thus give too high a number. Schaak[2] recommends the following method of separation:—Dissolve the borocalcite as indicated above. Filter and make the solution up to 500 c.c. Nearly neutralise 100 c.c. by titration with alkali, using methyl orange as indicator. Add 2 to 3 grms. of barium carbonate (free from alkali), warm on a steam bath for half an hour. Cool, filter, wash and titrate the filtrate with alkali as indicated above. The first method may give values 1·5 per cent. too high, while Schaak's modification will furnish values 0·15 per cent. too high.

Jacobi's Process for Determining Alkalies in the Presence of Borates.[3]—The alkalies in borates may be rapidly evaluated by digesting, say, 2 grms. in hydrochloric acid and evaporating the solution to dryness for silica. Add dilute hydrochloric acid, boil, filter and wash the silica; precipitate the iron and

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[1] Methyl orange or methyl red may be used instead of the nitrophenol with satisfactory results.

[2] M. F. Schaak, *Journ. Soc. Chem. Ind.*, **23**, 699, 1904.

[3] K. Jacobi, *Journ. Amer. Chem. Soc.*, **26**, 88, 1904.

alumina by means of ammonia; lime by ammonium oxalate; and magnesia by ammonium phosphate. Remove the excess of phosphate by means of pure ferric chloride, and remove the excess of the latter by ammonia. Evaporate the solution twice to dryness with concentrated nitric acid, using 40 c.c. of the acid for the first evaporation and 20 c.c. for the second. Then evaporate with excess of hydrochloric acid. Take up the residue with water and evaporate to dryness again in a platinum dish. Heat the residue to dull redness to drive off the water and the ammonium salts. Cool and weigh as anhydrous boric oxide, sodium (with possibly potassium) chloride and regenerated sodium borate. Dissolve the residue in hot water, cool and determine the soda present as borate by titration with 0·5N-sulphuric acid, using methyl orange as indicator. Titrate the neutralised solution for total boric oxide with 0·5N-sodium hydroxide, using phenolphthalein as indicator in the presence of excess of glycerol. Sum the boric oxide and the soda so obtained, and subtract the result from the weight of the residue in the platinum dish. The difference is said to be "sodium chloride," from which the sodium oxide is calculated by multiplying the amount of sodium chloride by 0·5303. If potassium [1] salts and sulphates be present, their amounts are determined in separate portions. Processes like these can, of course, only give approximate results by a balancing of errors.

Lunge's Process.—In analysing boronatrocalcite, Lunge [2] dissolved the mineral in dilute hydrochloric or nitric acid, and precipitated the lime as calcium oxalate and the magnesia as phosphate. The three bases—lime, soda and magnesia—are determined by adding a known volume of standard (hydrochloric or nitric) acid, and titrating the excess of acid with standard alkali, as indicated for borax. Deduct the results found for lime and magnesia, and the difference represents the soda. [3] Water is determined as the "loss on ignition." The difference represents the boric oxide and impurities. In one case, Kraut found 6·72 per cent. of sodium chloride and 4·74 per cent. of sodium sulphate [4] in a sample of boronatrocalcite.

§ 321. The Determination of Boric Oxide in Silicates— Wherry's Process.

(a) Sullivan and Taylor's Modification.

Methods for the determination of boric oxide in silicates containing alumina and iron, by fusing the sample with alkali carbonate, removing the silica and basic oxides with ammonio-zinc oxide, Schaffgotsch's or Seeman's solutions (page 727), and finally precipitating the boric oxide as an insoluble borate —magnesium,[5] barium,[6] calcium [7] or silver [8] borate, or potassium boro-

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[1] Or remove the boric oxide by repeated evaporation with methyl alcohol (page 664), and determine the potash and soda in the usual way.

[2] G. Lunge, *Liebig's Ann.*, **138**, 51, 1866; *Chem. News*, **15**, 86, 214, 1867; K. Kraut, *Liebig's Ann.*, **139**, 52, 1866. According to Lunge, there is no need to remove the boron as fluoride, since the results with and without the removal of boron "entirely coincide within the ordinary limits of error."

[3] Potash is said to be rarely present.

[4] H. How, *Chem. News*, **15**, 192, 1867; F. Wöhler, *ib.*, **16**, 15, 1867.

[5] C. Marignac, *Zeit. anal. Chem.*, **1**, 405, 1862.

[6] P. von Berg, *Zeit. anal. Chem.*, **16**, 25, 1877; H. N. Morse and W. M. Burton, *Amer. Chem. Journ.*, **10**, 154, 1888.

[7] A. Ditte, *Ann. Chim. Phys.*, (5), **4**, 549, 1875; *Compt. rend.*, **80**, 490, 561, 1875; A. Joly, *ib.*, **100**, 103, 1885.

[8] A. P. J. du Mênil, *Berzelius' Jahresber.*, **9**, 180, 1829.

fluoride,[1]— are not satisfactory, because part of the boric oxide is retained very tenaciously by the precipitated alumina. Wherry's method [2] was based on Schaak's process and it provided a useful method of approximation when the time needed for the more elaborate and tedious distillation process was not available.

Subsequent work, upon which the following details are based, has eliminated some of the more serious weaknesses of the process and has considerably increased its accuracy.

Fusion.—Half a gram of the analysis sample is fused with 3 grms. of sodium carbonate and the heating continued for a couple of minutes after a state of quiet fusion has been reached.[3] The cold cake is removed from the crucible to a beaker of boron-free glass, not more than 20 to 30 c.c. of water being used in the transference. The mass is gently simmered over a small flame until the cake is entirely disintegrated and, after settling, the supernatant liquid is filtered under suction through a Gooch crucible. The residue is boiled up with three successive small quantities of distilled water and the supernatant liquid filtered off after each extraction. The filtrates and washings are transferred to a 250 c.c. round-bottomed flask of boron-free glass and about 7 c.c. of concentrated hydrochloric acid and a few drops of nitric acid added. The solution is gently boiled under a reflux condenser until all reaction ceases.
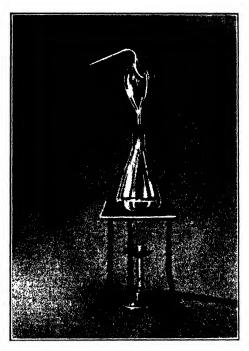
Fig. 141.—Boiling with "Splash Trap."

Removal of Iron and Aluminium.—A moderate excess of pure, dry calcium

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[1] A. Stromeyer, *Liebig's Ann.*, **100**, 82, 1856; G. Krüss and H. Moraht, *ib.*, **260**, 180, 1896; F. Wöhler, *ib.*, **141**, 268, 1867; C. Bodewig, *Chem. News*, **50**, 49, 1884; *Zeit. anal. Chem.*, **23**, 149, 1884; C. Thaddéeff, *ib.*, **36**, 568, 1897; H. Rose, *Pogg. Ann.*, **80**, 262, 1850; C. Rammelsberg, *ib.*, **80**, 466, 1880; J. J. Berzelius, *ib.*, **2**, 118, 1824.

[2] E. T. Wherry, *Journ. Amer. Chem. Soc.*, **30**, 1687, 1908; J. M. Lindgren, *ib.*, **37**, 1137, 1915; E. C. Sullivan and W. C. Taylor, *Journ. Ind. Eng. Chem.*, **6**, 897, 1914; W. W. Scott *et al.*, *ib.*, *Anal. Ed.*, **4**, 306, 1932; H. L. Payne, *ib.*, **6**, 45, 1934; P. Nicolardot and J. Boudet, *Bull. Soc. chim.*, (4), **21**, 97, 1917; J. D. Cauwood and T. E. Wilson, *Journ. Soc. Glass Tech.*, **2**, 246, 1918; V. Dimbleby and W. E. S. Turner, *ib.*, **7**, 76, 1923; V. Dimbleby, *ib.*, **14**, 51T, 1930; A. A. Machigin and T. F. Korzukhina, *Journ. Russ. Phys. Chem. Soc.*, **59**, 573, 1927; A. S. Dodd, *Analyst*, **54**, 715, 1929; L. Malaprade and J. Schnoutka, *Compt. rend.*, **192**, 1653, 1931; W. Mylius, *Chem. Ztg.*, **57**, 173, 1933; P. N. Grigoriev, *Keram. i Steklo*, **9**, 21, 1933; D. Klein, *Bull. Soc. chim.*, (2), **29**, 198, 1878; M. Hönig and G. Spitz, *Zeit. angew. Chem.*, **9**, 549, 1896; O. A. Kulskaya, *Zavodskaya Lab.*, **2**, 26, 1933; W. H. Chapin, *Journ. Amer. Chem. Soc.*, **30**, 1687, 1908.

[3] V. Dimbleby and W. E. S. Turner (*Journ. Soc. Glass Tech.*, **7**, 76, 1923) say that boric oxide is lost by volatilisation during fusion if the borosilicate contains more than about 10 per cent. of boric oxide. With materials rich in boric oxide they recommend the addition of pure silica to reduce the boric oxide content of the sample to about 10 per cent. Half a gram of the mixture is then fused up with 3 grms. of sodium carbonate.

carbonate is then *cautiously* added to the contents of the flask and the mixture well boiled under the reflux condenser for 10 minutes (or longer if necessary) to expel all the carbon dioxide and precipitate the iron and aluminium. The steam should not be allowed to rise more than half way up the condenser tube and, after boiling, the inside of the latter must be rinsed down into the flask. The supernatant liquid is filtered under suction through a small Buchner funnel and the residue in the flask extracted three times by boiling-up under the reflux condenser with successive small quantities of water.[1] Sullivan and Taylor state that by conducting all filtrations and washings under suction, the weakness of Wherry's method, *viz.* the retention of boric oxide by the precipitated aluminium and iron hydroxides, is overcome. The residue is finally transferred to the funnel and washed with a little hot water. The filtrate and washings are poured back into the flask, a small quantity of calcium carbonate is added and the mixture again boiled for ten minutes under the reflux condenser. The condenser is now replaced by a splash trap (fig. 141) and suction *gradually* applied.

The Titration.—When the liquid ceases to boil under the full suction of the pump, it is cooled to atmospheric temperature,[2] 2 grms. of mannitol are added and titration carried out with 0·1N-sodium hydroxide [3] using phenolphthalein as indicator.

(*b*) **Payne's Modification.**[4]

The initial procedure is identical with Sullivan and Taylor's process, except that the filtrate and washings from the fusion are boiled up with hydrochloric acid in a 250 c.c. *graduated* flask under the reflux condenser. After boiling, a strong solution of sodium hydroxide is added from a burette to the acid solution until the latter is nearly neutral but still shows an acid reaction to methyl red. Aluminium and iron hydroxides are precipitated just before neutrality is reached. The condenser is replaced and the liquid boiled gently for 15 minutes with the precautions previously mentioned in the alternative process. Payne states that under these conditions all the carbon dioxide is removed without loss of boron and the precipitated hydroxides occlude no boric oxide. After rinsing down the condenser tube, the flask is rapidly cooled without unduly exposing its contents to the air.[5] When cold, the flask is filled up to the mark with a solution of calcium hydroxide, the stopper is then inserted and the contents well shaken. The calcium hydroxide makes the solution alkaline without introducing any soluble carbonates and the last traces of aluminium and iron are precipitated. The liquid is rapidly filtered through a dry paper and funnel into a dry flask and, without washing the precipitate, two aliquot portions are at once pipetted out into flasks for titration in duplicate.

The Titration.—To each portion in turn add methyl red and just sufficient hydrochloric acid to give an acidic reaction. Now run in the standard sodium

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[1] Dimbleby (*l.c.*) dissolves the residue in the flask in a small excess of dilute hydrochloric acid, boils up and reprecipitates with a slight excess of calcium carbonate. In the presence of arsenic, antimony, tin, lead, zinc and manganese re-solution of the residue in hydrochloric acid, followed by a slight excess of sodium hydroxide solution, has been found to liberate satisfactorily the adsorbed boric oxide. After filtering, the filtrate is titrated as usual for boric oxide.

[2] If the precipitate is red (ferric oxide) the solution must be filtered before titration, but undue exposure to air must be avoided.

[3] Free from sodium carbonate.

[4] W. W. Scott *et al.*, *Ind. Eng. Chem. Anal. Ed.*, **4**, 306, 1932; H. L. Payne, *ib.*, **6**, 45, 1934.

[5] A soda lime guard tube can be used to protect the contents of the flask from atmospheric carbon dioxide.

hydroxide solution from a burette until the indicator just turns a full lemon-yellow colour, then add an excess of mannitol and a couple of drops of phenolphthalein. Continue the titration until a permanent red colour is obtained which is not bleached by the further addition of mannitol.

Using 0·2N-alkali, Payne found that the variation between duplicate analyses on borate ores, containing from 29 to 44 per cent. of boric oxide, ranged from a maximum of 0·15 to 0 per cent. with an average difference of 0·07 per cent.

(c) Glaze and Finn's Process.

Glaze and Finn have described a method for the routine determination of boric oxide in silicates which is based upon the partition coefficient of boric oxide between ether and water.[1] The faintly acid solution from the fusion of the silicate is shaken up with ether and ethyl alcohol and the ether layer is then titrated for boric oxide. Under these conditions, i.e., in the presence of ethyl alcohol and hydrochloric acid, the partition coefficient of the boric oxide between the ethereal and aqueous layers is given as 0·403 at $25° \pm 2°$. The method is said to be accurate and rapid for 0·7 to 16 per cent. of boric oxide. Barium, fluorine and abnormal amounts of iron interfere slightly; zinc must be absent.

§ 322. The Determination of Boric Oxide in Silicates— Distillation Process.

If methyl alcohol be distilled from a mixture containing free boric acid, methyl borate, boiling at 55° to 56°, distils over. The methyl borate can be saponified with alkalies and the boric acid determined by gravimetric or volumetric processes. This reaction was simultaneously evolved by Gooch and by Rosenbladt in 1887, and it has since been extensively used [2] for the

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[1] F. W. Glaze and A. N. Finn, *Glass Ind.*, **17**, 156, 1936; *Journ. Soc. Glass Tech.*, **20**, A383, 1936.

[2] F. A. Gooch, *Amer. Chem. Journ.*, **9**, 23, 1887; K. Farnsteiner, *Zeit. Nahr. Genuss.*, **3**, 1, 1900; K. Windisch, *ib.*, **9**, 641, 1905; R. Fischer, *ib.*, **3**, 17, 1900; J. Wolff, *ib.*, **3**, 600, 1900; **4**, 157, 1901; J. J. Ebelmen and Bouquet, *Ann. Chim. Phys.*, (3), **17**, 54, 1846; J. J. Ebelmen, *ib.*, (3), **16**, 129, 1846; H. Schiff, *Liebig's Ann.*, *Suppl.*, **5**, 154, 1867; H. Schiff and E. Bechi, *Compt. rend.*, **61**, 697, 1865; H. Moissan, *ib.*, **116**, 1087, 1893; S. L. Penfeld and E. S. Sperry, *Amer. J. Science*, (3), **34**, 222, 1887; J. E. Whitfield, *ib.*, (3), **34**, 281, 1887; F. A. Gooch and L. C. Jones, *ib.*, (4), **7**, 34, 1899; C. E. Cassal, *Analyst*, **15**, 230, 1890; A. K. Reischle, *Zeit. anorg. Chem.*, **4**, 111, 1893; A. Mandelbaum, *ib.*, **62**, 364, 1909; H. Funk and H. Winter, *ib.*, **142**, 257, 1925; K. Kraut, *Zeit. anal. Chem.*, **36**, 165, 1897; T. Rosenbladt, *ib.*, **26**, 21, 1887; W. Strecker and E. Kannappel, *ib.*, **61**, 378, 1922; E. Schulek and G. Vastagh, *ib.*, **84**, 167, 1931; **87**, 165, 1932; A. W. Blyth, *Proc. Chem. Soc.*, **15**, 51, 1899; C. Montemartini, *Gazz. Chim. Ital.*, **28**, i, 344, 1898; G. H. Beermann, *Kritische Studien über die neueren quantitativen Bestimmungsmethoden der Borsäure mit Einschluss der Turmalin-analyse*, Berlin, 1898; J. Prescher, *Arch. Pharm.*, **242**, 194, 1904; A. Schneider and C. Gaab, *Pharm. Centr.*, **37**, 672, 1896; W. H. Low, *Chem. News*, **95**, 52, 61, 73, 1907; *Journ. Amer. Chem. Soc.*, **28**, 807, 1906; W. H. Chapin, *ib.*, **30**, 1691, 1908; G. W. Sargent, *ib.*, **21**, 858, 1899; L. de Koningh, *ib.*, **19**, 55, 1897, O. von Spindler, *Schweizer Wochenschrift Chem. Pharm.*, **43**, 659, 1906; *Chem. Ztg.*, **29**, 566, 1905; R. Arndt, *ib.*, **33**, 725, 1909; C. Aschman, junr., *ib.*, **40**, 460, 1916; H. Copaux and G. Boiteau, *Bull. Soc. chim.*, (4), **5**, 217, 1909; G. Bertrand and H. Agulhon, *ib.*, (4), **7**, 125, 1910; H. Moissan, *ib.*, (3), **11**, 955, 1894; H. Fromme, *Tschermak's Mitt.*, **28**, 329, 1910; E. Polenske, *Arbeit. Kaiser. Gesund.*, **17**, 564, 1900; **19**, 167, 1902; A. Gunther, *ib.*, **19**, 489, 1902; G. Raulin, *Monit. Scient.*, (5), **1**, 434, 1911; G. Halpen, *Ann. Falsif.*, **8**, 1, 1915; E. T. Allen and E. G. Zies, *Journ. Amer. Cer. Soc.*, **1**, 739, 1918; L. A. Congdon and J. M. Rosso, *Chem. News*, **129**, 219, 1924; S. Moriyasu, *Researches Electrotech. Lab. Japan*, No. 153, 1925; L. V. Wilcox, *Ind. Eng. Chem. Anal. Ed.*, **2**, 358, 1930; G. Vastagh, *Magyar Chem. Fol.*, **37**, 55, 1931; **38**, 17, 1932; I. P. Alimarin and I. I. Romm, *Trans. Inst. Econ. Mineral* (*U.S.S.R.*), **53**, 5, 1932; C. Sumuleanu and G. Ghimicescu, *Bul. Soc. Chim. România*, **15**, 79, 1933; M. F. Schaak, *Journ. Soc. Chem. Ind.*, **23**, 699, 1904.

determination of boric oxide in silicates and alumino-silicates. Ethyl alcohol can be used,[1] but it forms ethyl borate, boiling at 118°–119°. In consequence of the higher boiling-point of ethyl borate, methyl alcohol,[2] though more expensive, is more effective than ethyl alcohol.

Preparation of the Sample for Distillation.—Fuse 0·5 grm.[3] of the sample with 6 grms. of sodium carbonate (page 144). When the crucible is cold, decompose the cake[4] in the crucible gradually by the addition of sufficient hydrochloric acid (1 in 1)—about 20 c.c. will be needed—to neutralise the excess of sodium carbonate used in the fusion. Care must be taken to avoid loss by spurting. Transfer the resulting solution to a 250 c.c. flask. The flask is then fitted with a reflux condenser (fig. 140), and boiled for an hour in order to drive off the carbon dioxide. The reflux condenser is to prevent loss due to volatilisation of boric acid with the issuing steam. *Aqueous solutions of boric acid must never be boiled in open vessels when the boric acid is to be determined quantitatively.* Wash the condenser tube with a little water and collect the runnings in the flask. Pour the liquid into a 250 c.c. distillation flask (*A*, fig. 142). Now add granular anhydrous calcium chloride to the solution. About 1 grm. of the salt per c.c. of liquid will suffice. Rotate the flask for a few minutes in order to ensure a thorough mixing of the contents. In adding the calcium chloride, keep the neck of the flask clean. The object of the calcium chloride is to prevent the hydrolysis of the methyl borate in the flask, and thus facilitate its removal. Sulphuric or phosphoric acid can also be used as dehydrating agents.[5]

The Distillation Apparatus.—An apparatus similar to that indicated in fig. 142 is fitted up. *A* is a 250 c.c. distilling flask[6] containing the boric acid solution, prepared as indicated above. *B* is a 500 to 800 c.c. distilling flask containing methyl alcohol free from acetone.[7] Owing to violent bumping which occurs when methyl alcohol is boiled in glass vessels, a boiling tube[8] is

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[1] H. Rose, *Pogg. Ann.*, 80, 262, 1846.

[2] Avoid the use of impure methyl alcohol, which blackens or evolves sulphur dioxide when heated with sulphuric acid on a water bath. See footnote 7.

[3] For substances containing a high proportion of boric oxide, 0·25 grm. may be used. The total boric oxide should be kept below 0·1 grm., otherwise the distillation will require a long time, the titration will require a large volume of solution and the end-point will be less distinct. If metals likely to injure the platinum crucible are present, the substance may be fused in a porcelain crucible (felspathic glaze), and the crucible and cake powdered and treated as described in the text.

[4] The first residue from the Smith's process for alkalies may be dried and then used for this determination.

[5] If strong acids be used for the distillation, and if chlorides be present, chlorine may be evolved. In that case, it is well to remove the chlorine by precipitation with silver nitrate and proceed with the distillation at once. Excess silver nitrate, if desired, can be removed by precipitation with sodium hydroxide or carbonate. Similar remarks apply to the presence of nitrates, oxalates, citrates and tartrates (but not acetates) when the distillation is made from concentrated sulphuric acid in place of the calcium chloride indicated in the text. For Rosenbladt's suggestion to use silver sulphate in the flask, see page 618.

[6] Boron-free glass should be used. Some varieties of glass contain boric oxide and are consequently a source of danger. A Lewkowitsch's flask (J. Lewkowitsch, *Journ. Chem. Soc.*, 55, 360, 1889; G. George, *Chem. News*, 78, 259, 1898) with a wide delivery tube may be used.

[7] Pure methyl alcohol can be obtained by saturating the commercial product at its boiling-point with chlorine. The chlorinated liquid is stood over quicklime to remove excess of chlorine and then fractionated through a column. The fraction boiling round about 65° is collected.

[8] BOILING TUBES.—This important auxiliary is a simple and effective means of preventing the bumping of most liquids during boiling. The boiling tube here described appears to have been first suggested by D. Gernez (*Compt. rend.*, 86, 472, 1878; H. Scudder, *Journ. Amer. Chem. Soc.*, 25, 163, 1903; *Chem. News*, 88, 242, 1903). It is made as follows:—Draw out
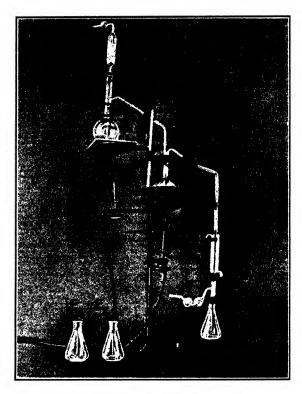
Fig. 142.—Distillation Apparatus.

a piece of glass tubing until its internal bore is from 0·5 to 1·0 mm. diameter. The tube is sealed (c, fig. 143) about 1 cm. from one end, a, by holding the tube in the flame until the sides have run together. Cut the tube the desired length—say, 16 cm.—and seal the end b to prevent the entrance of liquid. The upper end of the boiling tube should reach very nearly to the top of the flask. The tube is placed open end down in the liquid. The open end a should rest on the bottom near the hottest part of the flask and remain there during the boiling. Hence, the tube should be heavy enough to prevent its displacement from the

Fig. 143.—Boiling Tube.

bottom. For liquids of high specific gravity, therefore, it may be necessary to use a piece of thick-walled capillary tubing with a wide bore (maybe up to 5 mm.); for frothing liquids and liquids of low boiling-point, a narrow boiling tube is best.

The action of the boiling tube is as follows:—The air in ac expands and passes through the liquid in small bubbles. The air is gradually replaced by the vapour of the liquid being boiled, and the stream of bubbles is continuous so long as the temperature about the end ac is at the boiling-point of the liquid. This prevents superheating and explosive boiling. The seal c should be below the surface of the liquid, even if it be necessary to bend the portion ab for the purpose and make ac nearly parallel with the bottom of the flask; otherwise vapour will condense in ac, which would stop the stream of bubbles. The flame should be protected from draughts so that the temperature of the liquid does not fall below its boiling-point and thus cause the capillary to fill with liquid. The boiling tube is useless if it be filled with liquid. Hence it should be cold and empty when placed in the flask. The liquid is shaken out of the boiling tube each time it is used. G. Torossian, *Journ. Amer. Chem. Soc.*, **36**, 513, 1914. For the prevention of bumping by the use of flasks with a lining of fused-in ground glass, see A. V. Morton, *Ind. Eng. Chem. Anal. Ed.*, **6**, 384, 1934.

necessary each time the flask is used. C is a small Fresenius' gas washer [1] containing a little mercury. This acts as a safety valve should the tube leading from B to A get clogged. C can be fitted with a long exit tube to carry the vapours of alcohol away from the proximity of the flame should alcohol blow out. D is a Lendrich's condenser.[2] E is a 250 c.c. Erlenmeyer's flask to act as a receiver. It is fitted with a tube F containing enough water to act as a water seal and prevent the loss of methyl borate during the distillation. From three to four receiving flasks, E_1, E_2, E_3, are used, and all fit on the same stopper G. The connections are made as indicated in the diagram.

The Distillation.—The flask B is heated and methyl alcohol vapour distils into the flask A. When about 25 c.c. of alcohol have condensed in A, the latter flask is heated [3] sufficiently to prevent any further condensation of alcohol vapour in A. The distillation must not proceed too rapidly or methyl borate may be lost through the water trap. When about 100 c.c. of distillate have been collected, change the receiver. Transfer the contents of the trap F to the flask just removed. Add a drop of p-nitrophenol [4] to the same flask and run in the standard soda solution until the free acid is neutralised. To titrate for boric acid, add 1 c.c. of phenolphthalein to the neutralised solution and titrate until the pink coloration has developed. The end-point is not very sharp, owing to the action of the alcohol on the indicator. The difference between the burette readings with the two indicators gives an approximation to the amount of boric acid in the distillate. Add to the distillate twice as much standard alkali as was used in the phenolphthalein titration for boric acid. If 5 c.c. of alkali were required for the boric acid titration, add 10 c.c. of the same alkali. The object of adding the excess of alkali is to prevent loss of boric acid [5] when the alcohol is distilled off later on. When another 100 c.c. has collected in the second Erlenmeyer flask, change the receiver and treat the distillate as before. If less than 1 c.c. of 0.1N-sodium hydroxide be required, or 0.2 c.c. of 0.5N-sodium hydroxide be required, for the boric acid titration, the distillation is completed. If more than this amount of alkali be required, continue the distillation a third and maybe a fourth time. If sufficient calcium chloride has been used, the second distillation is usually sufficient.[6]

The following readings were made during a determination of the boric oxide in 0.5 grm. of glaze:—

0.5N-NaOH used. Indicator.	First distillate.	Second distillate.	Third distillate.	Total.
p-Nitrophenol . . .	2·7	0·3	0·2	3·2
Phenolphthalein . . .	4·1	0·4	0·1	4·6

Hence, in all, 4·6 c.c. of the 0.5N-NaOH solution were used for the boric acid in the phenolphthalein titration. Add 9·2 c.c. of the 0.5N-NaOH in order to fix the boric acid during the next stage of the operation.

[1] R. Fresenius, *Zeit. anal. Chem.*, 15, 62, 1876.
[2] K. Lendrich, *D.R.G.M.*, 198543, 1903; F. Allihn, *Zeit. anal. Chem.*, 25, 36, 1886.
[3] In a paraffin bath H; the thermometer J shows the temperature of the paraffin bath.
[4] L. V. Wilcox (*Ind. Eng. Chem. Anal. Ed.*, 2, 358, 1930) prefers methyl red.
[5] According to E. Polenske (*Arbeit. Kaiser. Gesund.*, 17, 564, 1900), a mixture of soda and boric acid corresponding with $5Na_2O.4B_2O_3$ is stable in boiling methyl alcohol.
[6] Instead of passing the vapour of methyl alcohol through the boric acid solution, B and C may be eliminated and a stoppered separating funnel fixed in A—as in the original Gooch's apparatus. Then add liquid methyl alcohol in separate portions 10 c.c. at a time. Six additions then usually suffice (G. W. Sargent, *Journ. Amer. Chem. Soc.*, 21, 858, 1899).

Removal of Methyl Alcohol from the Distillate.—The alkaline distillates are now poured into a flask which is connected to a condenser through a swan-neck. Use as little water as possible for the rinsing. A boiling tube is placed in the flask and the flask is heated. The alcohol which distils off is collected in a receiver placed below the condenser.[1] When the alcohol has distilled off, the residue should occupy about 25 c.c. If less, make up to approximately this volume with distilled water. Add diluted hydrochloric acid (1 : 1) drop by drop until the colour of both indicators is just discharged, but carefully avoid any excess of acid. Put a boiling tube into the flask and heat the solution on the steam bath for about two minutes. The flask is then connected with the filter pump and the liquid allowed to cool while the pump is in action. This decomposes any carbonates and there is no danger of losing boric oxide. The liquid should be colourless, hot or cold. If otherwise, sufficient acid is not present.

Final Titration of the Boric Oxide.—Neutralise any excess of acid with 0·5N-sodium hydroxide until the yellow tint of the nitrophenol appears. Make the solution acid with 0·1N-hydrochloric acid and again neutralise with 0·1N-alkali until a faint yellow colour appears. The solution is now exactly neutral and one drop of 0·1N-acid should discharge the colour of the indicator. Now add 1 grm. mannitol (or 40 c.c. of glycerol) and titrate with 0·1N- or 0·5N-alkali according to the amount of boric oxide present (the "methyl alcohol" titration shows this), as indicated under boric acid.

With the sample previously discussed, the following readings were made:—23·6 c.c. of 0·1N-NaOH were required. 1 c.c. of the 0·1N-NaOH corresponded with 0·003322 grm. B_2O_3.[2] Hence, $23·6 \times 0·003322 = 0·0784$ grm. B_2O_3 was present per 0·5 grm. of the glaze; or the glaze contained 15·68 per cent. of boric oxide—B_2O_3.

Test Experiments.—Determinations with artificial mixtures of known amounts of boric oxide with sodium silicate; alum; potassium fluoride; ferric and ferrous salts; arsenious, zinc, stannous and antimonous salts; salts of the alkalies and alkaline earths, gave quite satisfactory results. 0·0350 grm. of boric oxide was used in the following determinations with three different mixtures of the substances just enumerated:

First distillate (100 c.c.) required .	2·2	1·9	1·9	c.c. 0·5N-NaOH.
Second distillate (100 c.c.) required	0·4	0·5 [3]	0·3	c.c. 0·5N-NaOH.
Total B_2O_3 found	0·0348	0·0346	0·0352	grm.

Hence, it is inferred that the substances above enumerated did not interfere with the volatilisation of the boric oxide, nor with its accurate titration afterwards.[4]

Other Methods of Collecting the Methyl Borate.—Instead of decomposing the distillate with sodium hydroxide as indicated above, Thaddéeff[5] collected the distillate in a solution of caustic potash and subsequently precipitated the boric

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[1] The alcohol may be recovered by distillation from quicklime and 100 c.c. of a concentrated solution of caustic soda. The distillate should give no reaction for boric acid.

[2] The 0·1N-NaOH was standardised against boric acid.

[3] A third distillate (100 c.c.) contained the equivalent of 0·0005 grm. B_2O_3.

[4] According to E. T. Allen and E. G. Zies (*Journ. Amer. Cer. Soc.*, **1**, 739, 1918), arsenious oxide affects the results and must be rendered innocuous by oxidation with hydrogen peroxide. Large amounts of fluorides are likewise said to impair the accuracy. The distillation process does not work in the presence of tungstates—H. Copaux and G. Boiteau, *Bull. Soc. chim.*, (4), **5**, 217, 1909.

[5] C. Thaddéeff, *Zeit. anal. Chem.*, **36**, 568, 1897.

acid as potassium borofluoride; Rosenbladt [1] hydrolysed the methyl borate with magnesia; Gooch [2] used calcium oxide for the same purpose. In the two latter cases the contents of the distilling flask were acidified with nitric or acetic acid (Gooch), or a non-volatile acid—sulphuric (Rosenbladt) or phosphoric (Gladding) [3] acid. The magnesia, being insoluble, does not act very rapidly, and lime is difficult to calcine to a constant weight on account of its tendency to absorb carbon dioxide and moisture. Hehner used disodium phosphate [4]; Aschman,[5] ammonium phosphate; Schneider and Gaab,[6] sodium carbonate; Stolba,[7] borax; and Gooch and Jones,[8] sodium tungstate (approximately 5 grms. per 0.1 grm. B_2O_3). The last-named substance has the advantage of being easily obtained pure and it is soluble in water, so that the hydrolysis proceeds comparatively quickly.[9]

§ 323. Determination of Silica and Alumina in Boro-silicates.

In the analysis of silicates containing boric oxide, only part of the boric oxide is lost during the two evaporations to dryness; the other part of the boric oxide is precipitated with the alumina and iron. This gives high results.[10] To eliminate the boric oxide in the silica evaporations, add 20 c.c. of *pure* [11] methyl alcohol, or better (Jannasch) [12] methyl alcohol saturated with hydrogen chloride, to the solution before each evaporation to dryness. This ensures the complete elimination of the boric oxide as methyl borate.

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[1] T. Rosenbladt, *Zeit. anal. Chem.*, **26**, 21, 1887; *Chem. News*, **55**, 18, 101, 1887.

[2] F. A. Gooch, *Amer. Chem. Journ.*, **9**, 23, 1887; *Chem. News*, **55**, 7, 1887; C. Marignac, *Zeit. anal. Chem.*, **1**, 406, 1862; K. Kraut, *ib.*, **36**, 165, 1897; S. L. Penfield and E. S. Sperry, *Amer. J. Science*, (3), **34**, 220, 1887; L. A. Congdon and J. M. Rosso, *Chem. News*, **129**, 219, 1924. A gram of lime, for instance, is weighed and evaporated to dryness with the methyl borate after ignition. The increase in weight represents boric oxide. The solid "crawls" badly during the evaporation, and the methyl alcohol "bumps" badly if it is allowed to boil.

[3] T. S. Gladding, *Journ. Amer. Chem. Soc.*, **20**, 258, 1898; M. F. Schaak, *Journ. Soc. Chem. Ind.*, **23**, 699, 1904; H. Lührig, *Pharm. Centr.*, **42**, 50, 1901. C. Fresenius and O. Popp (*Zeit. öffent. Chem.*, **3**, 155, 188, 1897) used anhydrous sodium sulphate.

[4] O. Hehner, *Analyst*, **16**, 141, 1891.

[5] C. Aschman, *Chem. Ztg.*, **40**, 460, 1916; L. A. Congdon and J. M. Rosso, *Chem. News*, **129**, 219, 1924.

[6] A. Schneider and C. Gaab, *Pharm. Centr.*, **37**, 672, 1896.

[7] F. Stolba, *Journ. prakt. Chem.*, (2), **90**, 457, 1863; R. J. Manning and W. R. Lang (*Journ. Soc. Chem. Ind.*, **26**, 803, 1907) precipitate the boric oxide in the distillate by barium chloride and weigh as $Ba(BO_2)_2$.

[8] F. A. Gooch and L. C. Jones, *Amer. J. Science*, (4), **7**, 34, 1899; *Chem. News*, **79**, 99, 111, 1899.

[9] The sodium tungstate, freed from carbonate by fusion with a little tungstic acid, is weighed in a platinum dish and then placed in the Erlenmeyer's flask E_1 (fig. 142). After the distillation, methyl alcohol is boiled off and the contents are transferred to the same platinum dish as was used for weighing the sodium tungstate. Evaporate to dryness, fuse as before, cool and weigh. The increase in weight represents the boric oxide.

[10] F. Wöhler, *Liebig's Ann.*, **141**, 268, 1867; R. Fresenius and E. Hintz, *Zeit. anal. Chem.*, **28**, 324, 1889; W. Hampe, *Chem. Ztg.*, **15**, 521, 1891.

[11] See footnote 7, page 660.

[12] P. Jannasch, *Zeit. anorg. Chem.*, **12**, 208, 1896; *Zeit. anal. Chem.*, **36**, 383, 1897.

CHAPTER XLI.

THE DETERMINATION OF PHOSPHORUS.

An accurate determination of phosphoric oxide, by whatever method it is made, requires much skill and not a little practice. The advocate of one method often makes the other suffer in comparison, more by reason of his own want of skill in the manipulation of the method than by reason of any great advantage inherent in his own.—A. A. BLAIR.[1]

§ 324. The Detection of Phosphorus.

PHOSPHORUS in the form of phosphoric oxide is normally detected in qualitative work by the formation of a canary yellow precipitate of ammonium phosphomolybdate in nitric acid solution. If only traces of phosphorus be present, a yellow solution but no precipitate is obtained.[2] Silica in solution gives a similar coloration and, consequently, the test is not specific.

Feigl's Test.[3]—Place a drop of the solution on a *quantitative* filter-paper and add one drop of ammonium molybdate solution,[4] containing 15 per cent. of tartaric acid. Dry over a small flame for 30 seconds. Add one drop of a saturated solution of benzidine in acetic acid and then hold the paper over an open ammonia bottle. A blue colour indicates the presence of phosphoric oxide. As little as 0·0015 mgrm. P_2O_5 can be detected, and the interference of considerable amounts of arsenate, borate or silicate is prevented by the addition of the tartaric acid. To detect phosphates in minerals, rocks and slags,[5] a little of the powdered substance is placed on a filter-paper, or on a scratch on a porcelain plate, and the above test applied. A blank test should be made on the filter to see if it is free from phosphates.

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[1] A. A. Blair, *Chem. News*, **56**, 246, 1887.
[2] G. Vortmann (*Zeit. anal. Chem.*, **56**, 465, 1917) says that if a solution of molybdic acid be used, containing pyridine instead of nitric acid, the sensitivity of the test is increased ten-fold. P. Medinger (*Chem. Ztg.*, **39**, 781, 1915) adds a saturated solution of strychnine nitrate to 100 c.c. of a 40 per cent. solution of ammonium molybdate until the first-formed precipitate no longer dissolves. The resulting solution is poured into an equal volume of nitric acid (sp. gr. 1·4). The mixture is stood for 18 hours and then filtered. Twenty drops of this reagent will give a turbidity with 10 c.c. of a solution containing 0·25 mgrm. P_2O_5 per litre.
[3] F. Feigl, *Zeit. anal. Chem.*, **61**, 454, 1922; **74**, 386, 1928; **77**, 299, 1929; F. Frey, *Chem. Ztg.*, **48**, 281, 1924. Compare F. Feigl, *Mikrochem.*, **2**, 186, 1924; B. Angeli, *Chem. Zentr.*, (2), **95**, 1931.
[4] AMMONIUM MOLYBDATE SOLUTION.—R. Fresenius, *Anleitung zur qualitativen chemischen Analyse*, Braunschweig, 107, 1919. Dissolve 150 grms. of the salt in a litre of water and add a litre of nitric acid (sp. gr. 1·2). Let the liquid stand for several days in a warm place, then decant from any precipitate of ammonium phosphomolybdate and preserve for use.
[5] H. Leitmeyer, *Mikrochem.*, **6**, 144, 1928.

§ 325. The Properties of Ammonium Phosphomolybdate.

The methods for the determination of phosphorus have probably been the subject of more investigations than any other analytical process.[1] The subject, though clarified a little, is by no means definitely settled, since a number of contradictory statements confront the analyst. These can only be decided in the laboratory, but the very fact that the phenomena connected with this determination have led to a number of contradictions is a remarkable testimony to the obscurity of the reactions involved. In the valuation of phosphates by chemists selected by buyer and by seller, we have been informed that differences involving 10–15 per cent. of the total cost of the materials were at one time by no means uncommon; and many analytical chemists were accordingly classed by sellers and buyers as "high" and "low" analysts.[2] The buyer naturally favoured the "low" analyst; the seller, the "high" analyst. The differences, in most cases, were probably due to the need for standard methods of analysis, particularly in dealing with so imperfect and faulty a method of analysis as was then in vogue.

In 1851, Sonneschein showed that the reaction between ammonium molybdate and orthophosphoric acid, discovered by Svanberg and Struve[3] three years earlier, could be used for the quantitative determination of phosphorus. The precipitation of the orthophosphoric acid[4] takes place in the presence of iron, aluminium, lime, magnesia and the alkalies.

The yellow ammonium phosphomolybdate is but sparingly soluble in water. According to Chesneau,[5] 0·030 grm. of the ammonium phosphomolybdate dissolves in a litre of water at 15°. This means that if a litre of water comes in contact with the precipitate, 0·030 grm. will pass into solution.

Action of Nitric Acid.—Hundeshagen represents the reaction between ammonium molybdate and, say, sodium phosphate by the equation:

$$Na_3PO_4 + 12(NH_4)_2MoO_4 + 26HNO_3 = (NH_4)_3PO_4 . 12MoO_3 . 2HNO_3 . H_2O \\ + 3NaNO_3 + 21NH_4NO_3 + 11H_2O$$

where 1 grm. of phosphoric anhydride—P_2O_5—corresponds with 23 grms. of nitric acid—HNO_3. But the amount of nitric acid can be increased considerably beyond this amount without interfering with the precipitation. If, however, the quantity of the nitric acid rises above 71 grms. HNO_3 per gram of P_2O_5,

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[1] For a review of methods, see A. Korevaar, *Chem. Weekb.*, **12**, 814, 1915; A. F. da Silva, *Rev. Chim. Pura Appl.*, (3), **5**, 69, 1930.

[2] A. E. Davies, *Chem. News*, **23**, 220, 1871. See J. M. McCandless and J. Q. Burton, *Ind. Eng. Chem.*, **16**, 1267, 1924.

[3] L. Svanberg and H. Struve, *Journ. prakt. Chem.*, (1), **44**, 257, 1848; H. Struve, *ib.*, (1), **54**, 288, 1851; L. Sonneschein, *ib.*, (1), **53**, 339, 1851; H. Rose, *Pogg. Ann.*, **76**, 26, 1849.

[4] If meta- or pyro-phosphoric acids be present, they should be digested with, say, potassium permanganate or chromic acid. If a brown precipitate of manganese peroxide be produced, insoluble in acids, a small quantity of potassium nitrite will clear the solution. The manganese dioxide is reduced to MnO, which dissolves in the acid. Nitric acid and potassium chlorate are not always vigorous enough to convert the meta- and pyro- to ortho-phosphoric acid. C. Meineke and E. F. Wood, *Rev. Univ. Mines*, (3), **9**, 235, 1890; M. A. von Reis, *Stahl Eisen*, **9**, 1025, 1889; **10**, 1059, 1890.

[5] G. Chesneau, *Rev. Met.*, **5**, 237, 1908; G. de Lucchi, *Russ. Min.*, **32**, 21, 1910; *Tables annuelles*, **1**, 381, 403, 1910; V. Eggertz, *Journ. prakt. Chem.*, (1), **79**, 496, 1860; F. Hundeshagen, *Chem. News*, **60**, 169, 177, 188, 201, 205, 1889; *Zeit. anal. Chem.*, **28**, 164, 1889; **32**, 144, 1893; R. Fresenius, *ib.*, **3**, 446, 1864; G. Jörgensen, *ib.*, **45**, 273, 1906; *Analyst*, **34**, 372, 1909; *Mem. Acad. Roy. Soc. Danemark*, (7), **2**, 141, 1905; *Zeit. angew. Chem.*, **24**, 542, 1911; R. Finkener, *Ber.*, **11**, 1638, 1878. Some say that the solubility of the precipitate is decreased, and some say that the solubility is increased, by the addition of ammonium nitrate.

the precipitate of ammonium phosphomolybdate will be partially decomposed and the precipitation will consequently be incomplete. If over 1700 grms. of HNO_3 per gram of P_2O_5 be present, no ammonium phosphomolybdate will be precipitated. Both hydrochloric and sulphuric acids act more powerfully than nitric acid.[1] In consequence, *nitric acid gives the widest margin of safety between a sufficient quantity and an overdose of acid.* The solvent effects of an overdose of nitric acid can be overcome by adding an excess of molybdate. The greater the excess of acid, the greater the amount of molybdate needed for the complete precipitation of the phosphate. Chesneau gives the solubility of ammonium phosphomolybdate in dilute nitric acid as follows :

Table LX.—Solubility of Ammonium Phosphomolybdate in Nitric Acid.

Nitric acid.	Ammonium phosphomolybdate dissolved per 100 c.c. acid.
Per cent.	Grm. at 15°.
0	0·0030
1	0·0371
5	0·0682
10	0·0901

This table shows that nitric acid augments the solubility of the precipitated ammonium phosphomolybdate.

Action of Ammonium Nitrate.—Chesneau gives the solubility of ammonium phosphomolybdate in aqueous solutions of ammonium nitrate as follows :

Table LXI.—Solubility of Ammonium Phosphomolybdate in Aqueous Solutions of Ammonium Nitrate.

Ammonium nitrate.	Ammonium phosphomolybdate dissolved per 100 c.c. solution.
Per cent.	Grm. at 15°.
0	0·0030
5	0·0099
10	0·0113

This shows an increase in the solubility of ammonium phosphomolybdate in the presence of ammonium nitrate. In the absence of ammonium nitrate, the precipitate is inclined to separate in a colloidal condition which is exceedingly difficult to filter clear. Hundeshagen showed that this will occur if less than 0·5 per cent. of ammonium nitrate be present in the solution. The precipitate, even when this amount is present, settles slowly. In order to get rapidly settling precipitates, from 5 to 15 per cent. of ammonium nitrate should be present in the solution. Besides accelerating the rate of settling, ammonium nitrate also accelerates the rate of precipitation and ensures a more complete

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[1] For the influence of sulphates, see P. L. Hibbard, *Journ. Ind. Eng. Chem.*, 5, 998, 1913; K. G. Falk and K. Sugiura, *Journ. Amer. Chem. Soc.*, 37, 1507, 1915; A. Bäule, W. Riedel and K. Täufel, *Zeit. Untersuch. Lebensm.*, 67, 274, 1934; M. Ishibashi, *Mem. Coll. Sci. Kyoto*, A12, 135, 1929.

precipitation with a smaller excess of ammonium molybdate.[1] These facts are illustrated by the following numbers. The conditions in the different experiments were otherwise the same.

Table LXII.—*Effect of Ammonium Nitrate on the Precipitation of Ammonium Phosphomolybdate.*

Ammonium molybdate.	Amount of P_2O_5 precipitated.	
	No nitrate.	10 grms. of nitrate.
c.c.		
50	0·1100	0·1165
60	0·1156	0·1160
70	0·1155	0·1160
80	0·1158	0·1162
90	0·1165	0·1163

Hence, 50 c.c. of a given solution of ammonium molybdate will precipitate all the phosphoric acid in a given solution in the presence of ammonium nitrate, under conditions where 5·6 per cent. may escape precipitation in the absence of the ammonium nitrate.

Influence of Temperature.—The precipitate forms rather more quickly in hot solutions. According to Hundeshagen, if the ammonium phosphomolybdate be precipitated in the cold, it separates in the form of rounded grains of different sizes, which settle very slowly. Such precipitates are inclined to choke the pores of the filter-paper and retard filtration. If the precipitation occurs in hot solutions, the ammonium phosphomolybdate separates in the form of octahedral crystals (usually grouped "rosettenförmig"), which settle rapidly and filter easily. The precipitate formed in hot solutions is also easier to wash. If the temperature of the solution be above 60°, white needles of ammonium tetramolybdate, $(NH_4)_2O.4MoO_3.2H_2O$, may be produced by prolonged heating, and this the more, the higher the temperature and the longer the solution is heated. Ammonium tetramolybdate is soluble in water and nitric acid, but is precipitated by ammonium nitrate. When ammonium tetramolybdate is once formed, it will contaminate the precipitate even if the ammonium phosphomolybdate be dissolved and precipitated a second time. Hence, in order to avoid this source of error,[2] the solution should not be heated too long a time, nor at too high a temperature.

Composition of the Precipitate.—The actual composition of the precipitate depends upon the time of standing, temperature and the nature of the mother

[1] E. Richters, *Zeit. anal. Chem.*, 10, 471, 1871; C. Stunkel, T. Wetzke and P. Wagner, *ib.*, 21, 353, 1882; F. Hundeshagen, *ib.*, 28, 141, 1889; C. Gilbert, *Correspondenz Ver. anal. Chem.*, 1, 1878; S. W. Johnson, *Journ. Amer. Chem. Soc.*, 16, 462, 1894; G. E. F. Lundell and J. I. Hoffman, *Ind. Eng. Chem.*, 15, 44, 1923.

[2] In illustration of the different ideas which prevail as to the time and temperature of heating required for complete precipitation, the following may be quoted:—R. Fresenius (*Zeit. anal. Chem.*, 3, 446, 1864)—6 hrs. at 65°; R. Fresenius (*Anleitung zur quantitativen chemischen Analyse*, Braunschweig, 1, 411, 1875)—12 hrs. at 40°; O. Abesser, W. Jani and M. Märcker (*Zeit. anal. Chem.*, 12, 254, 1873)—4 to 6 hrs. at 50°; C. Stünkel, T. Wetzke and P. Wagner (*ib.*, 21, 353, 1882)—1 hr. at 80° to 90°; P. Pietsch, W. Rohn and P. Wagner, (*ib.*, 19, 444, 1880); W. R. Mummery (*Analyst*, 43, 324, 1918)—30 mins. at 60°; R. de Roode, *Journ. Amer. Chem. Soc.*, 17, 43, 1895; M. Fleischer and K. Müller, *Journ. Landw.*, 20, 96, 1875.

liquid. This partly explains how so many different factors have been proposed for converting the weight of the precipitate into the equivalent "P_2O_5." Thus, factors varying from 3·02 per cent. P_2O_5 (Sonneschein) to 4·39 per cent. (Debray) have been suggested. The following selection [1] will illustrate the different results which have been obtained for the composition of the yellow ammonium phosphomolybdate:

	Rammelsberg.	Sonneschein.	Gibbs.	Gladding.
H_2O	5·77	}11·18	3·94	2·44
NH_4	3·25		3·35	2·44
P_2O_5	3·90	3·02	3·66	3·76
MoO_3	86·45	86·08	89·05	91·36

Obviously, if the precipitation be not performed under definite conditions, there is some uncertainty as to the composition of the precipitate. Hence, the precipitate is frequently redissolved in ammonia and reprecipitated in the form of ammonium magnesium phosphate, or as ammonium phosphomolybdate.

Chesneau [2] has studied this phase of the subject. He found that when ammonium nitrate is absent, the precipitate weighs less than theory requires, and this the more with solutions containing small amounts of phosphorus. When ammonium nitrate is present, the precipitate with solutions poor in phosphorus is heavier than theory requires. As a matter of fact, the precipitate is not always a single compound, but a mixture of different substances— ammonium phosphomolybdate, molybdic acid, ammonium tetramolybdate and occluded ammonium molybdate.[3] When ammonium nitrate is absent, the amount of molybdic acid in the precipitate increases with increasing concentration of the phosphoric acid, up to a certain definite limit. When ammonium nitrate is present, the amount of molybdic acid increases as the amount of phosphorus decreases. When no molybdic acid crystals are present, as will be the case when about 0·005 grm. of phosphorus is present, the stellate crystals of ammonium phosphomolybdate predominate. If the amount of phosphorus be reduced to 0·00027 grm., the precipitate will be contaminated with triclinic crystals of ammonium tetramolybdate.

Influence of Ammonium Salts.—Fresenius [4] has shown that the presence of

[1] C. Rammelsberg, *Ber. Berl. Akad.*, 573, 1877; *Ber.*, 10, 1776, 1877; R. Finkener, *ib.*, 11, 1638, 1878; L. Sonneschein, *Journ. prakt. Chem.*, (1), 53, 339, 1851; M. Seligsohn, *ib.*, (1), 67, 470, 1856; V. Eggertz, *ib.*, (1), 79, 490, 1860; W. Gibbs, *Amer. Chem. Journ.*, 3, 317, 406, 1881; *Proc. Amer. Acad.*, 18, 232, 1883; 21, 96, 1886; *Chem. News*, 45, 29, 1882; H. Debray, *ib.*, 17, 183, 1868; *Compt. rend.*, 66, 702, 1868; S. Posternak, *ib.*, 170, 930, 1920; D. J. Hissink and H. van der Waerden, *Chem. Weekblad*, 2, 179, 1905; G. A. Spiess, *Viertelj. Pharm.*, 9, 257, 1860; M. Nutzinger, *ib.*, 4, 549, 1855; J. König, *Landw. Vers. Stat.*, 10, 401, 1868; A. Villiers and F. Borg, *Bull. Soc. chim.*, (3), 9, 486, 1893; *Compt. rend.*, 116, 989, 1893; H. C. Babbitt, *Journ. Anal. App. Chem.*, 7, 165, 1893; A. von Lipowitz, *Pogg. Ann.*, 109, 135, 1860; C. Friedheim, *Zeit. anorg. Chem.*, 4, 275, 1893; T. Salzer, *Liebig's Ann.*, 187, 322, 1877; G. P. Baxter and R. C. Griffin, *Amer. Chem. Journ.*, 34, 204, 1905; T. S. Gladding, *Journ. Amer. Chem. Soc.*, 18, 23, 1896.

[2] G. Chesneau, *Rev. Met.*, 5, 237, 1908; *Principes théoriques et pratiques d'Analyse minérale*, Paris, 233, 1912; M. Ishibashi, *Mem. Coll. Sci. Kyoto*, A12, 135, 1929; S. Kitajima, *Sci. Papers Inst. Phys. Chem. Tokyo*, 16, 285, 1931.

[3] G. P. Baxter, *Amer. Chem. Journ.*, 28, 298, 1902.

[4] R. Fresenius, *Zeit. anal. Chem.*, 3, 446, 1864; R. Fresenius, C. Neubauer and E. Luck, *ib.*, 10, 133, 1871; G. König, *ib.*, 10, 305, 1871; E. Richters, *Dingler's Journ.*, 199, 183, 1871; G. E. F. Lundell and J. I. Hoffman, *Ind. Eng. Chem.*, 15, 44, 1923. For the separation of phosphorus and arsenic, see J. Courtois, *Journ. Pharm. Chim.*, (8), 23, 269, 404, 1936; A. Tettamanzi, *Atti Accad. Sci. Torino, Classe Sci. Fis. Mat. Nat.*, 71, 125, 1936.

ammonium chloride retards the precipitation,[1] and Richters has shown that the presence of ammonium sulphate acts in a similar manner. In these cases, a larger excess of ammonium molybdate must be added, or the results will be low.

Influence of Iron Salts.—If ferric salts be present, a comparatively large excess of ammonium molybdate is needed, even in the presence of ammonium nitrate; and if too little acid be present, a reddish crust which does not readily dissolve in ammonia may be formed. This is due to the formation of a ferric phosphomolybdate.[2] According to Meineke, a larger excess of nitric acid is also needed if much iron be present in the solution, in order to prevent the precipitation of iron with the ammonium phosphomolybdate; and Jüptner [3] proposes to use 6 per cent. of tartaric acid with the molybdate solution in order to prevent the precipitation of the iron.

Influence of Titanium and Vanadium.—The presence of titanium retards the precipitation of ammonium phosphomolybdate. For instance, two solutions, each containing the equivalent of 0·140 grm. of ammonium phosphomolybdate, gave the following results:

Titanic acid (equivalent of)	.	.	0·008	0·016 grm.
Ammonium phosphomolybdate	.	.	0·122	0·118 grm.

Hence, there is a deficiency of 13 per cent. of P_2O_5 even in the presence of but 0·008 grm. of titanic acid. Pattinson [4] separates the titanium [5] before precipitating the phosphorus, in the following way:—Reduce the ferric to ferrous sulphate; add a saturated solution of ammonium alum and then an excess of ammonia. The precipitate contains aluminium phosphate, aluminium hydroxide and titanic oxide. Fuse the washed and ignited precipitate with sodium carbonate and extract the fused mass with water. Sodium phosphate and aluminate dissolve, while sodium titanate remains insoluble. "As a rule, one fusion suffices to separate all the phosphoric acid from the titanic acid." Conversely, Lundell and Hoffman [6] say that phosphorus can be accurately determined, even in the presence of a fifty-fold excess of titanium, by preliminary precipitation as phosphomolybdate, prior to conversion to magnesium pyrophosphate. Difficulties may arise, however, when much titanium or zirconium is present, owing to the separation of titanium or zirconium phosphate during solution of the material. In such cases the insoluble residue is filtered off and fused with sodium carbonate, as in Pattinson's method.

Vanadium is carried down quantitatively by the phosphomolybdate precipitate, which has then different properties from the ordinary precipitate,

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[1] C. Meineke (*Chem. Ztg.*, **20**, 113, 1896) says that ammonium chloride does not retard the precipitation.

[2] G. Chesneau, *Rev. Met.*, **5**, 237, 1908; G. Arth, *Bull. Soc. chim.*, (3), **2**, 324, 1890; *Chem. News*, **62**, 155, 1890; C. Meineke, *Rep. Anal. Chem.*, **6**, 304, 1886; E. Wolff, *Zeit. anal. Chem.*, **3**, 94, 1864; R. Fresenius, *ib.*, **3**, 446, 1864; P. Schweitzer, *ib.*, **9**, 85, 1870; J. V. Janovsky, *ib.*, **11**, 157, 1872; S. W. Johnson, *Journ. Amer. Chem. Soc.*, **16**, 462, 1894; L. von Szell, *Landw. Vers. Stat.*, **55**, 341, 1901; E. H. Archibald and H. B. Keegan, *Trans. Roy. Soc. Canada*, **10**, 67, 1916.

[3] R. Woy, *Chem. Ztg.*, **21**, 470, 1897; H. F. von Jüptner, *Oester. Zeit. Berg. Hütt.*, **42**, 471, 1894; A. Villiers and F. Berg, *Compt. rend.*, **116**, 989, 1893; A. von Endrédy, *Zeit. anorg. allgem. Chem.*, **194**, 239, 1930.

[4] J. and H. S. Pattinson, *Journ. Soc. Chem. Ind.*, **14**, 443, 1895; P. H. Waller, *Journ. Amer. Chem. Soc.*, **20**, 513, 1898; C. Baskerville, *Journ. Anal. Appl. Chem.*, **7**, 194, 1893.

[5] In silicate analyses, titanium phosphate separates with the silica during the evaporation for silica.

[6] G. E. F. Lundell and J. I. Hoffman, *Ind. Eng. Chem.*, **15**, 171, 1923.

for it is more soluble in nitric acid and in the ordinary washing solutions.[1] If vanadium be present, it is reduced to the quadrivalent state by the addition of 2 to 3 c.c. of 10 per cent. ferrous sulphate solution (phosphorus-free) and a few drops of sulphurous acid. The phosphomolybdate is then precipitated from the reduced solution at a temperature not exceeding 20°.[2]

Influence of Arsenic Oxide.—If arsenic be present and the temperature of the solution be too high, ammonium arsenomolybdate will contaminate the precipitate of ammonium phosphomolybdate, and, later on, the second precipitate. A temperature of 45° is generally considered a safe upper limit,[3] but if much arsenic be present, the phosphomolybdate precipitate will even then be contaminated. For instance, Jörgensen found the following amounts of arsenic in the precipitated phosphomolybdate after standing 24 hours at 37°:

Original solution contained . 0·0033   0·0066   0·0143 grm. arsenic acid.
Precipitate contained . . 0·0013   0·0029   0·0040 grm. arsenic acid.

It is therefore advisable to remove the arsenic, if present, either by means of hydrogen sulphide (Fresenius) or by evaporation with hydrochloric and oxalic acids (Campbell).[4]

Influence of Silica.—It is generally agreed that silica should be removed, since it is liable to be precipitated in the form of ammonium silicomolybdate,[5]

[1] H. Brearley and F. Ibbotson, *The Analysis of Steel-Works Materials*, London, 163, 1902; J. R. Cain and J. C. Hostetter, *Journ. Ind. Eng. Chem.*, 4, 250, 1912.

[2] J. R. Cain and F. H. Tucker, *Journ. Ind. Eng. Chem.*, 5, 647, 1913; W. O. Robinson, *ib.*, 8, 148, 1916; G. E. F. Lundell and J. I. Hoffman, *ib.*, 15, 171, 1923; R. A. Gortner and W. M. Shaw, *Soil Sci.*, 2, 299, 1916. Copper, molybdenum, aluminium, chromium and nickel do not interfere: arsenic, tin, titanium and tungsten do, and must be removed. G. W. Gray and C. D. Garbutt (*Journ. Iron Steel Inst.*, 111, 395, 1925; *Engineering*, 119, 717, 1925) precipitate phosphorus as magnesium ammonium phosphate in the presence of citric acid when vanadium is present. F. W. Kriesel (*Chem. Ztg.*, 47, 177, 1923) removes vanadium as vanadyl ferrocyanide and then separates the phosphate in the filtrate by precipitation with ammonia in the presence of ammonium alum.

[3] H. C. Babbitt, *Journ. Amer. Chem. Soc.*, 6, 381, 1884; J. O. Handy, *ib.*, 16, 231, 1894; M. Frank and F. W. Hinrichsen, *Stahl Eisen*, 28, 295, 1908; M. Seligsohn, *Journ. prakt. Chem.*, (1), 67, 481, 1856; H. Seyberth, *Ber.*, 7, 391, 1874; W. Gibbs, *Amer. Chem. Journ.*, 7, 313, 1886; E. D. Campbell, *Journ. Anal. App. Chem.*, 2, 370, 1888; B. Moreau, *Journ. Pharm. Chim.*, (5), 26, 157, 1892.

[4] R. Fresenius, *Anleitung zur quantitativen chemischen Analyse*, Braunschweig, 1, 421, 1875; E. D. Campbell, *Journ. Anal. App. Chem.*, 7, 2, 1893; G. Jörgensen, *Mem. Acad. Roy. Soc. Danemark*, (7), 2, 141, 1905; P. Champion and H. Pellet, *Bull. Soc. chim.*, (2), 27, 6, 1877; *Chem. News*, 35, 115, 1877; G. Maderna, *Atti Accad. Lincei*, 19, 15, 1910; G. W. Gray and C. D. Garbutt, *Journ. Iron Steel Inst.*, 111, 395, 1925; *Engineering*, 119, 717, 1925; G. E. F. Lundell and J. I. Hoffman, *Ind. Eng. Chem.*, 15, 44, 171, 1923.

[5] T. Petersen, *Verhandl. Geol. Reichsanst.*, 80, 1869; W. Knop, *Chem. Centr.*, 2, 691, 861, 1857; R. Fresenius, *Anleitung zur quantitativen chemischen Analyse*, Braunschweig, 1, 411, 1875; J. H. Vogel, *Repert. Anal. Chem.*, 7, 469, 568, 1887; E. Richters, *Dingler's Journ.*, 199, 183, 1871; R. W. Atkinson, *Chem. News*, 35, 127, 1877. On the other hand, E. Thilo (*Chem. Ztg.*, 11, 193, 1887), E. R. E. Müller (*ib.*, 35, 1201, 1911), E. H. Jenkins (*Journ. prakt. Chem.*, (2), 13, 237, 1876), G. Kennepohl (*Chem. Ztg.*, 11, 1089, 1887), C. Meineke (*Repert. Anal. Chem.*, 6, 303, 325, 1886), J. Hanamann (*Zeit. Landw. Vers. Ost.*, 3, 53, 1900), and H. C. Sherman and H. S. J. Hyde (*Journ. Amer. Chem. Soc.*, 22, 652, 1900) consider that no notice need be taken of the silica. For *the separation of phospho- and silico-molybdates*, see P. G. Mélikoff, *Compt. rend.*, 154, 1478, 1912. The method is to digest the molybdate precipitate with "permolybdate reagent" four times during 24 hours. The phosphomolybdate passes into solution, while the silicomolybdate remains insoluble. Filter. Destroy the hydrogen peroxide by heating, and precipitate the phosphoric acid in the filtrate as usual. The "permolybdate reagent" is made by mixing equal volumes of 30 per cent. hydrogen peroxide and an 8 per cent. solution of ammonium molybdate in nitric acid. The method is also used for *the separation of phosphoric and colloidal silicic acids*—P. G. Mélikoff and M. Becaia, *Compt. rend.*, 154, 775, 1912; *Chem. Ztg.*, 36, 617, 1912; P. G. Mélikoff, *Journ. Russ. Phys. Chem. Soc.*, 44, 605, 1912.

which contaminates the phosphomolybdate and, incidentally, does not settle so quickly as the latter compound. According to Isbert and Stutzer,[1] the silicomolybdate can be removed from the phosphomolybdate by washing with ice-cold water, in which the former is easily soluble, the latter almost insoluble. The silica is, however, usually removed by evaporation before the separation of the phosphorus.

Influence of Fluorine.—Fluorine delays the formation of the precipitate of ammonium phosphomolybdate and gives rise to errors in the determination. It can be removed by the addition of borax and evaporation of the solution.[2]

Influence of Organic Matter.—Carbonaceous matter is generally supposed to hinder the precipitation of the ammonium phosphomolybdate precipitate [3]; so also are the organic acids—tartaric and oxalic. Jüptner, however, says that this is not the case, and even recommends the addition of tartaric acid with the ammonium molybdate solution to retard the precipitation of the iron.

§ 326. The Gravimetric Determination of Phosphorus —Woy's Process.

Woy's method [4] of separating phosphorus in the form of ammonium phosphomolybdate is one of the best. The phosphoric oxide in an aliquot portion [5] of the acid solution of the pyrosulphate fusion, or from the silica separation, obtained in the regular course of the typical silicate analysis (page 168) may be determined by this process; or separated by Joulie's process (page 682), and determined colorimetrically.

An aliquot portion,[6] say 100 c.c., of the solution of the pyrosulphate fusion (page 168) is neutralised with ammonia and evaporated, if necessary, to about 50 c.c.[7] Add concentrated ammonia until a precipitate forms which does not disappear on standing; add, say, 5 c.c. of concentrated nitric acid; add, say, 15 c.c. of ammonium nitrate solution,[8] so that the solution has between 5 and 15 per cent. of ammonium nitrate.[9] Place a thermometer in the liquid. Heat the solution to about 70°. Raise the thermometer about 2 inches above the level of the liquid in the beaker and pour rapidly into the solution, say,

[1] A. Isbert and A. Stutzer, *Zeit. anal. Chem.*, **26**, 583, 1887; *Chem. News*, **57**, 211, 1888.

[2] F. W. Neuhaus, *Zeit. anal. Chem.*, **104**, 416, 1936.

[3] F. Hundeshagen, *Zeit. anal. Chem.*, **28**, 164, 1889; J. König, *ib.*, **10**, 305, 1871; E. Richters, *Dingler's Journ.*, **199**, 183, 1871; V. Eggertz, *Journ. prakt. Chem.*, (1), **79**, 496, 1860; H. F. von Jüptner, *Oester. Zeit. Berg. Hütt.*, **42**, 471, 1894; R. Woy, *Chem. Ztg.*, **21**, 470, 1897; C. Reichard, *ib.*, **27**, 833, 1903; R. Hamilton, *Journ. Soc. Chem. Ind.*, **10**, 904, 1891; G. Maderna, *Atti Accad. Lincei*, **19**, 827, 1910; A. Tamm, *Chem. News*, **49**, 208, 1884; M. Schild, *Chimiste*, **3**, 25, 1912; M. Ishibashi, *Mem. Coll. Sci. Kyoto*, **A12**, 135, 1929; A. von Endrédy, *Zeit. anorg. allgem. Chem.*, **194**, 239, 1930.

[4] R. Woy, *Chem. Ztg.*, **21**, 441, 469, 1897; A. H. Maude, *Chem. News*, **101**, 241, 1910; G. B. van Kampen, *Chem. Weekblad*, **3**, 376, 1906; F. Hinden, *Zeit. anal. Chem.*, **54**, 214, 1915; J. Clarens, *Compt. rend.*, **166**, 259, 1918; *Bull. Soc. chim.*, (4), **25**, 87, 1919; W. R. Mummery, *Analyst*, **43**, 324, 1918; G. Jörgensen, *ib.*, **51**, 61, 1926; G. E. F. Lundell and J. I. Hoffman, *Journ. Ind. Eng. Chem.*, **15**, 44, 171, 1923; V. A. Beckley and A. Marais, *Journ. S. African Chem. Inst.*, **6**, 35, 1923; W. F. Pond, *Chemist-Analyst*, **45**, 16, 1925; M. Ishibashi, *Mem. Coll. Sci. Kyoto*, **A12**, 135, 1929; S. Kitajima, *Sci. Papers Inst. Phys. Chem. Tokyo*, **16**, 285, 1931; W. J. Skilling and E. D. Ballantine, *Journ. Soc. Chem. Ind.*, **48**, 115T, 1929.

[5] Or in the portion used for the determination of iron or titanium.

[6] If possible, no more solution should be taken than is equivalent to 0·1 grm. of P_2O_5. If more than this amount be present, take an aliquot portion and dilute to, say, 50 c.c.

[7] Most other solutions are treated in a similar manner. Arsenic is assumed to be absent.

[8] AMMONIUM NITRATE SOLUTION.—Dissolve 320 grms. of ammonium nitrate in water and make the solution up to a litre (4E).

[9] The following table gives the relative proportions of ammonium molybdate, nitric acid and ammonium nitrate to be used:—

10 c.c. of ammonium molybdate solution [1] down the stem of the thermometer, using it as a glass rod. Stir the liquid well. The yellow precipitate separates more thoroughly in hot solutions. Keep the solution at 70° for about half an hour. Decant through, say, a 7- or a 9-cm. filter-paper, and wash the precipitate [2] by decantation [3] (about six times) with a mixed solution (about 50 c.c.) of equal volumes of the ammonium molybdate solution, ammonium nitrate and nitric acid (1 : 2), until no permanent precipitate [4] separates from a drop of the wash-liquid on standing.[5] The precipitate is now distributed between the beaker and the filter-paper. Place the beaker with the precipitate beneath the funnel and dissolve the precipitate on the filter-paper with dilute ammonia (2·5 per cent.). If all the precipitate in the beaker does not dissolve, pour more ammonia into the beaker.[6] Wash the filter-paper half a dozen times

Table LXIII.—Composition of Mother Liquid for the Precipitation of Ammonium Phosphomolybdate.

P_2O_5.	Ammonium molybdate.	Ammonium nitrate.	Nitric acid.
grm.	c.c.	c.c.	c.c.
0·1	120	30	19
0·01	15	20	10
0·005	15	20	10
0·002	10	15	5
0·001	10	15	5

When 0·5 grm. of substance is in question, every per cent. of P_2O_5 in the original sample requires 5 c.c. of the molybdate solution (F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, 361, 1911). See also S. Kitajima, *Sci. Papers Inst. Phys. Chem. Tokyo*, 16, 285, 1931; M. Ishibashi, *Mem. Coll. Sci. Kyoto*, A12, 135, 1929.

[1] AMMONIUM MOLYBDATE SOLUTION.—Dissolve 34·34 grms. of ammonium heptamolybdate —3(NH_4)$_2$O.7MoO_3.4H_2O—in water and make the solution up to a litre ($\frac{1}{6}$E). 1 c.c. is nearly equivalent to 0·001 grm. P_2O_5. It is better to make the solution as needed; old solutions should not be used. The yellow deposit found in old solutions of ammonium molybdate is hydrated molybdic acid, H_2MoO_4.H_2O—A. R. Penfold, *Austral. Pharm. Notes and News*, 13, 17, 1917. Note that the ammonium molybdate of commerce is not (NH_4)$_2MoO_4$, but (NH_4)$_6Mo_7O_{24}$.4H_2O. The gradual precipitation of molybdic acid is avoided by storing the solution in green glass bottles to cut off heat rays from light—W. Heike, *Stahl Eisen*, 29, 1446, 1909. For the properties of molybdate solutions, see papers cited above and A. L. Winton, *Journ. Amer. Chem. Soc.*, 18, 445, 1896; M. Kupferschläger, *Bull. Soc. chim.*, (2), 36, 644, 1881; E. E. Mains, *Chemist-Analyst*, 11, 23, 1914.

[2] In washing, the yellow precipitate often has a tendency to crawl above the top of the paper. Hence, the paper should fit the funnel closely, so that the portion which crawls will not be lost.

[3] There is no need to transfer all the precipitate from the beaker to the filter-paper when a second precipitation is to be made.

[4] Pure water decomposes the precipitate. If a yellow precipitate should separate in the washings on standing, all the phosphorus was not precipitated. In that case, the filtered liquid must be treated with more ammonium molybdate, filtered and the precipitate washed again. A *white* precipitate of molybdic acid or ammonium tetramolybdate can be ignored.

[5] E. Raben (*Zeit. anal. Chem.*, 47, 546, 1908) washes until the wash-water gives no precipitate with potassium ferrocyanide. J. M. McCandless and J. Q. Burton (*Ind. Eng. Chem.*, 16, 1267, 1924) wash with a 5 per cent. solution of ammonium nitrate until the washings give no reaction for molybdenum when tested with hydrogen sulphide.

[6] If the liquid in the beaker remains turbid, acidify with nitric acid, add a small crystal of citric acid and, finally, ammonia until the liquid is alkaline. If the liquid be still turbid, filter, ignite the residue in a platinum crucible and fuse with a little sodium carbonate. Digest the cake with water, filter, acidify the filtrate with nitric acid, boil, make ammoniacal and add to the rest of the solution. See G. E. F. Lundell and J. I. Hoffman, *Ind. Eng. Chem.*, 15, 44, 171, 1923.

with the ammonia solution. The liquid in the beaker will now occupy about 50–100 c.c. It contains practically all the phosphoric acid, some molybdic acid and ammonium nitrate in ammoniacal solution.[1] The phosphorus may be determined in several different ways. Reprecipitation as ammonium magnesium phosphate or as ammonium phosphomolybdate will give satisfactory results.[2]

Alternative Procedure.—The following process for precipitating the phosphorus differs in some details from that outlined above. It gives excellent results. Dissolve 2·5 grms. of ammonium molybdate in 12·5 c.c. of water and add one drop of concentrated ammonia. Pour the solution into 12·5 c.c. of concentrated nitric acid. The mixed solution will precipitate 0·03 grm. of phosphorus; for larger quantities, proportionately increase the amount of precipitant taken (or decrease the weight of the sample used). The molybdate solution should be made up just before use. The phosphorus solution, which must be free from silica and hydrochloric acid, is just acidified with nitric acid and to it is added a 30 per cent. solution of ammonium nitrate at the rate of 15 c.c. for every 100 c.c. of phosphorus solution. Add the molybdate solution in the cold and then heat the mixture on a water bath but do not boil. Stir well and stand overnight.

§ 327. Reprecipitation as Ammonium Magnesium Phosphate.

Since Neubauer's researches, a considerable number of investigations has been made to determine the conditions whereby quantitative precipitation of magnesium ammonium phosphate can be ensured.[3] As mentioned on page 205, the danger is that the precipitate may be contaminated to a greater or smaller extent with normal magnesium phosphate, $Mg_3(PO_4)_2$, or with tetrammonium magnesium diphosphate, $Mg(NH_4)_4(PO_4)_2$, neither of which when once formed is readily converted into magnesium ammonium phosphate, $MgNH_4PO_4$. In particular, Balareff has thoroughly investigated this point

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[1] For the error due to phosphorus in the glass beakers, see A. Vita, *Stahl Eisen*, 32, 1352, 1912.

[2] RECOVERY OF MOLYBDENUM RESIDUES.—R. Fresenius, *Zeit. anal. Chem.*, 10, 204, 1871; F. Muck, *ib.*, 10, 307, 1871; 8, 377, 1869; O. Maschke, *ib.*, 12, 380, 1873; H. Uelsmann, *ib.*, 16, 52, 1877; E. Reichardt, *Arch. Pharm.*, (3), 2, 232, 1873; A. Gawalovski, *Chem. News*, 75, 98, 1897; *Oester. Chem. Ztg.*, 1, 385, 1898; H. Börntrager, *Zeit. anal. Chem.*, 33, 341, 1894; *Chem. News*, 70, 224, 1894; *Zeit. anal. Chem.*, 33, 341, 1894; M. M. Hoff, *Chemist-Analyst*, 8, 5, 1914; W. D. Brown, *Journ. Ind. Eng. Chem.*, 7, 213, 1915; C. G. Armstrong, *ib.*, 7, 764, 1915; P. Rudnick and R. D. Cooke, *ib.*, 9, 109, 1917; V. Lenher and M. P. Schultz, *ib.*, 9, 684, 1917; J. A. Prescott, *Analyst*, 40, 390, 1915; H. Kinder, *Stahl Eisen*, 36, 1094, 1916; R. Friedrich, *Chem. Ztg.*, 40, 560, 1916; 41, 674, 1917 ; A. Grête, *ib.*, 40, 813, 1916; H. Stamm, *ib.*, 40, 717, 1916; H. Rubricus, *ib.*, 40, 917, 1916 ; W. H. Lynas, *Met. Chem. Eng.*, 19, 169, 1918.

[3] H. Neubauer, *Ueber die Zuverlässigkeit der Phosphorsäurebestimmung als Magnesium-pyrophosphat*, Rostock, 1893; *Journ. Amer. Chem. Soc.*, 16, 289, 1894; K. K. Järvinen, *Zeit. anal. Chem.*, 43, 279, 1904; 44, 333, 1905; L. Moeser and G. Frank, *ib.*, 52, 346, 1913; Z. Karaoglanow, *ib.*, 57, 497, 1918; G. Jörgensen, *ib.*, 45, 273, 1906; 46, 370, 1907; 50, 337, 1911; 66, 209, 1925; *Analyst*, 34, 392, 1909; 51, 61, 1926; *Mem. Acad. Roy. Soc. Danemark*, (7), 2, 141, 1905; *Zeit. angew. Chem.*, 24, 542, 1911; L. W. Winkler, *ib.*, 32, 98, 1919 ; L. Desbourdeaux, *Bull. Sci. pharmacol.*, 27, 225, 300, 363, 1920; G. E. F. Lundell and J. I. Hoffman, *Ind. Eng. Chem.*, 15, 44, 171, 1923; J. M. McCandless and J. Q. Burton, *ib.*, 16, 1267, 1924; 19, 406, 1927; A. Travers and Mlle. Perron, *Ann. Chim.*, (10), 2, 43, 1924; F. L. Hahn, K. Vieweg and H. Meyer, *Ber.*, 60B, 971, 1927; B. W. Kilgore, *Journ. Amer. Chem. Soc.*, 16, 793, 1894; 17, 941, 1895; W. M. McNabb, *ib.*, 49, 891, 1927; 50, 300, 1928; N. Krilenko, *Arhiv Hemiju*, 2, 197, 1928; M. Ishibashi, *Mem. Coll. Sci. Kyoto*, A12, 23, 39, 49, 1929; J. I. Hoffman and G. E. F. Lundell, *U.S. Bur. Stand. Journ. Research*, 5, 279, 1930; H. Kleinmann, *Biochem. Zeit.*, 99, 19, 1919.

and concludes that a precipitate of the required composition can only be obtained by the method of Schmitz.[1]

The details of the recommended procedure are as follows:—The bulk of the ammonia in the ammoniacal solution of the phosphomolybdate precipitate is neutralised with hydrochloric acid. An excess of acid magnesia mixture [2] is added, followed by 5 grms. of ammonium acetate [3] and a few drops of phenolphthalein. The mixture is heated nearly to boiling and then a 2·5 per cent. solution of ammonia is run in from a burette with constant stirring until a turbidity is produced. On further stirring, the turbidity should disappear and the precipitate become crystalline within a minute. More ammonia is added until a pink coloration appears. Any precipitate on the stirring rod is washed off with 10 per cent. hydrochloric acid and more ammonia added until the pink colour reappears. When completely cooled, the solution is diluted with one-fifth its volume of concentrated ammonia (sp. gr. 0·88), stirred thoroughly, allowed to stand for a few minutes and then filtered. The precipitate is washed well with 2·5 per cent. ammonia solution, followed by two washings with absolute alcohol; after drying over a small flame, the precipitate is ignited to constant weight at 1100°.[4]

§ 328. Reprecipitation and Weighing as Ammonium Phosphomolybdate.[5]

To the ammoniacal solution of the ammonium phosphomolybdate (see § 326) add 20 c.c. of ammonium nitrate solution and 1 c.c. of ammonium molybdate solution, of the same concentrations as were used in the first precipitation [6] of the phosphomolybdate (pages 672–3). Heat the solution until gas bubbles begin to form and add 20 c.c. of hot 5 per cent. nitric acid gradually,

[1] D. Balareff, *Zeit. anorg. Chem.*, **101**, 229, 1917; **103**, 73, 1918; **104**, 53, 1918; **106**, 268, 1919; **117**, 91, 1921; B. Schmitz, *Zeit. anal. Chem.*, **45**, 512, 1906; **65**, 46, 1924.

[2] Schmitz (*l.c.*) recommends 30 c.c. of magnesia mixture for 0·1–0·55 grm. P_2O_5. ACID MAGNESIA MIXTURE.—Dissolve 56 grms. of magnesium chloride, $MgCl_2.6H_2O$, and 105 grms. of ammonium chloride in water. Filter, make acid to methyl orange with hydrochloric acid and dilute to a litre.

[3] To reduce the solubility of the magnesium ammonium phosphate—B. Schmitz (*l.c.*); W. M. McNabb (*l.c.*).

[4] The ignited precipitate should be white. J. M. McCandless and J. Q. Burton (*Ind. Eng. Chem.*, **19**, 406, 1927; F. Scheiding, *Zeit. angew. Chem.*, **8**, 79, 1895) moisten the precipitate on the Gooch crucible with ammonium nitrate solution before ignition in order to obtain a white residue. Traces of molybdic acid may contaminate the precipitate, even after a double precipitation—A. A. Blair, *Chem. News*, **56**, 246, 1887; A. Gawalovski, *Oester. Chem. Ztg.*, **1**, 385, 1890; J. M. McCandless and J. Q. Burton, *l.c.* W. Jones (*Journ. Biol. Chem.*, **25**, 87, 1916) recommends air drying and weighing as $MgNH_4PO_4.6H_2O$.

[5] A. Carnot, *Bull. Soc. chim.*, (3), **9**, 340, 1893; *Compt. rend.*, **116**, 106, 1893; A. Villiers and F. Borg, *Compt. rend.*, **116**, 989, 1893; *Journ. Pharm.*, **27**, 570, 1893; *Bull. Soc. chim.*, (3), **9**, 486, 1893; A. Villiers, *ib.*, (4), **23**, 305, 1918; N. von Lorenz, *Landw. Versuchs. Stat.*, **55**, 183, 1901; A. Stutzer, *ib.*, **94**, 251, 1919; N. von Lorenz, *Chem. Ztg.*, **32**, 707, 1908; *Oester. Chem. Ztg.*, **14**, 1, 1911; P. Christensen, *Zeit. anal. Chem.*, **47**, 529, 1908; H. Neubauer and F. Lücker, *ib.*, **51**, 161, 1912; O. Fallada, *Oesterr-ung Zeit. Zucker-Ind. Landw.*, **37**, 333, 1908; *Chem. Zentr.*, (2), **827**, 1908; F. Haussding, *Landw. Jahrb.*, **45**, 119, 1913; F. Haussding and O. Lemmermann, *ib.*, **46**, 327, 1914; *Chem. Zentr.*, (2), **506**, 1914; W. Holle, *Chem. Ztg.*, **38**, 1083, 1914; C. Reichard, *Pharm. Zentralhalle*, **52**, 1314, 1911; A. W. Clark and R. F. Keeler, *Journ. Ass. Off. Agric. Chem.*, **5**, 103, 1921; R. Kuhn, *Zeit. physiol. Chem.*, **129**, 64, 1923; M. Marqueyrol and L. Toquet, *Ann. Chim. anal.*, (2), **9**, 225, 1927; F. Holtz, *Biochem. Zeit.*, **210**, 252, 1929; M. Ishibashi, *Mem. Coll. Sci. Kyoto*, **A12**, 135, 1929; R. H. A. Plimmer, *Biochem. Journ.*, **27**, 1810, 1933; G. Jörgensen, *Zeit. anal. Chem.*, **108**, 190, 1937.

[6] The phosphorus should not be precipitated first by the magnesia mixture, but be first precipitated by the molybdate process. This ensures a definite amount of ammonia and ammoniacal salts in the solution, and thus leads to concordant results.

with constant stirring. After standing 3 to 4 hours, filter through a Gooch crucible and wash with 5 per cent. ammonium nitrate until no brown coloration is produced when a drop of the filtrate is brought in contact with a solution of potassium ferrocyanide. Dry[1] the yellow precipitate of $(NH_4)_3PO_4$. $12MoO_3.2HNO_3.H_2O$ in a current of air at $160°-180°$ in, say, a Paul's oven (fig. 87) to a constant weight,[2] and weigh as $(NH_4)_3PO_4.12MoO_3$.[3] In that case, the weight of the precipitate multiplied by 0.03783 represents the weight of the P_2O_5 in the sample taken for analysis.[4]

§ 329. Rapid Processes for Determining the Ammonium Phosphomolybdate.

In order to shorten the time required for the determination of phosphorus in terms of ammonium phosphomolybdate, the latter is often determined by a volumetric method. Pemberton's process[5] is in general use for the determination of small amounts of phosphorus in routine analyses. In this process

[1] E. Raben (Zeit. anal. Chem., 47, 546, 1908) finishes the washing with warm 70 per cent. alcohol; then with absolute alcohol; then with 10 c.c. of ether. He dries the precipitate at $110°-120°$, and weighs as $(NH_4)_3PO_4.12MoO_3$.

[2] The precipitate is somewhat hygroscopic, and the desiccator should have fresh concentrated sulphuric acid, not calcium chloride, otherwise the precipitate might gain in weight.

[3] If the precipitate appears green, add a small crystal of ammonium nitrate and re-heat, The precipitate then becomes uniformly yellow.

[4] If desired, the precipitate may be ignited to redness until the resulting $24MoO_3.P_2O_5$ has a homogeneous black colour. The ignited precipitate is not especially hygroscopic.

[5] J. Macagno, Gazz. Chim. Ital., 4, 567, 1874; Chem. News, 31, 197, 1875; A. Grete, Ber., 21, 2762, 1888; F. A. Emmerton, Trans. Amer. Inst. Min. Eng., 15, 93, 1886-7; T. M. Drown and P. W. Shimer, ib., 10, 137, 1881; P. W. Shimer, ib., 17, 100, 1888-9; T. M. Drown, ib., 18, 90, 1889; C. Jones, ib., 17, 411, 1888-9; 18, 705, 1889; Chem. News, 62, 220, 231, 1890; D. L. Randall, ib., 97, 113, 1908; Amer. J. Science, (4), 24, 313, 1907; O. F. von der Pfordten, Zeit. anal. Chem., 23, 432, 1884; A. Werncke, ib., 14, 1, 1875; H. Pemberton, Journ. Franklin Inst., 113, 184, 1882; Chem. News, 46, 4, 1882; Journ. Amer. Chem. Soc., 16, 278, 1894; A. A. Blair and J. E. Whitfield, ib., 17, 747, 1895; W. A. Noyes and E. D. Frohman, ib., 16, 533, 1894; C. B. Dudley and F. N. Pease, ib., 16, 224, 1894; R. A. Mahon, ib., 19, 792, 1897; O. S. Doolittle and A. Eavenson, ib., 16, 234, 1894; G. Auchy, ib., 18, 955, 1896; B. W. Kilgore, ib., 16, 765, 1894; 17, 741, 950, 1895; E. D. Campbell, Journ. Anal. App. Chem., 1, 370, 1887; B. W. Kilgore, Bull. U.S. Agric. Dept. (Chem.), 43, 68, 1894; G. P. Baxter, Amer. Chem. Journ., 28, 298, 1902; 34, 204, 1905; J. G. Fairchild, Journ. Ind. Eng. Chem., 4, 520, 1912. See page 451. E. Thilo, Chem. Ztg., 11, 193, 571, 1887; A. Isbert, ib., 11, 223, 1887; F. Hundeshagen, ib., 18, 445, 505, 547, 1894; E. H. Schultze, ib., 29, 508, 1905; J. O. Handy, Journ. Anal. Chem., 6, 204, 1892; Chem. News, 66, 324, 1892; Chem. Centr., (2), 185, 1892; H. Pemberton, Journ. Franklin Inst., 136, 362, 1893; 137, 304, 1894; Chem. Centr., (1), 105, 1894; Journ. Amer. Chem. Soc., 15, 382, 1893; 16, 278; 1894; 17, 178, 1895; B. W. Kilgore, ib., 16, 765, 1894; 17, 941, 950, 1895; 19, 703, 1897; W. A. Noyes and J. S. Royse, ib., 17, 129, 1895; F. P. Veitch, ib., 18, 389, 1896; C. B. Williams, ib., 17, 925, 1895; 23, 8, 1901; W. D. Richardson, ib., 29, 1314, 1907; P. B. Sircar, ib., 36, 2372, 1914; W. C. Day and A. P. Bryant, Journ. Franklin Inst., 137, 394, 1894; J. Ohly, Chem. News, 76, 200, 1897; J. Cézar, Bull. Assoc. Belge Chimistes, 16, 247, 1902; Chem. Centr., (2), 820, 1902; D. J. Hissink and H. van der Waerden, ib., (1), 1188, 1905; Chem. Weekb., 2, 179, 1905; D. J. Hissink, ib., 6, 181, 1909; G. H. G. Lagers, ib., 4, 632, 1907; Zeit. anal. Chem., 47, 561, 1908; F. Hundeshagen, ib., 28, 141, 1889; Zeit. öffent. Chem., 17, 283, 302, 322, 1911; L. T. Bowser, Amer. Chem. Journ., 45, 230, 1911; L. Wuyts, Ann. Chim. anal., 16, 134, 1911; J. G. Fairchild, Journ. Wash. Acad. Sci., 2, 114, 1912; P. L. Hibbard, Journ. Ind. Eng. Chem., 5, 998, 1913; P. McG. Shuey, ib., 9, 367, 1917; H. Heidenhain, ib., 10, 426, 1918; G. E. F. Lundell and J. I. Hoffman, ib., 15, 171, 1923; H. Kleinmann, Biochem. Zeit., 99, 95, 1919; M. B. Richards and W. Godden, Analyst, 49, 565, 1924; Rep. Amer. Soc. Testing Materials, Standards, 272, 1924; P. Nyssens Bull. Soc. chim. Belg., 34, 232, 1925; G. Hammarsten, Compt. rend. Lab. Carlsberg, 17, 1, 1928; V. Vincent, Ann. Falsif., 23, 475, 1930; M. Odin, Acta Paed., 9, 392, 1930; Chem. Zentr., (2), 802, 1931; L. Fricke, Stahl Eisen, 26, 279, 1906; J. A. Prescott, Journ. Agric. Science, 6, 111, 1914; G. C. Caldwell, Chem. News, 48, 61, 1883.

the precipitated phosphomolybdate is washed free from nitric acid and dissolved in a measured excess of standard alkali. The excess of alkali is titrated with standard acid with phenolphthalein as indicator.

The method is based on the assumption that the reaction between the phosphomolybdate and the alkali can be represented by the equation :—

$$(NH_4)_3PO_4.12MoO_3 + 23NaOH$$
$$= (NH_4)_2MoO_4 + 11Na_2MoO_4 + NaNH_4HPO_4 + 11H_2O$$

Thus the accuracy of the method primarily depends upon the precipitation of the phosphorus as a compound of definite and invariable composition and to ensure this, particular attention must be paid to the conditions of precipitation.

Hillebrand and Lundell[1] recommend the following procedure :—The phosphorus is precipitated as phosphomolybdate in the usual way (see page 672), but the temperature of precipitation must not exceed 40° to 45°, nor must the mixture be heated after the addition of the molybdate reagent. Shake the solution from time to time during 10 minutes in a stoppered flask (to avoid absorption of atmospheric carbon dioxide). Stand for 15 minutes and then decant through a small gravimetric paper, leaving as much as possible of the precipitate in the flask. Wash the walls of the flask and the precipitate five times with a 1 per cent. neutral solution of potassium nitrate. About 20 c.c. of solution should be used for each wash and the washings are poured through the filter-paper. Finally wash the filter-paper five times with 20 c.c. portions of the wash liquor, taking care to wash downwards from the edge to the apex of the paper and allowing the solution to filter completely between each washing. All free nitric acid should now have been removed from the walls of the flask, the precipitate and filter-paper. Transfer the filter-paper to the flask and add a measured excess of 0·1N-sodium hydroxide, free from carbonate. Dilute with 25 c.c. of water, stopper the flask and shake until the precipitate has all dissolved. Add about 100 c.c. of water and 6 drops of phenolphthalein. Titrate the solution with 0·1N-acid[2] until the pink colour of the indicator is just discharged. Finally add more 0·1N-sodium hydroxide until the pink colour reappears. The total volume of alkali added, less the volume of acid used in the titration, gives the volume of alkali reacting with the precipitated ammonium phosphomolybdate.

On the basis of the equation given above, 1 c.c. of 0·1N-sodium hydroxide is equivalent to 0·13487 mgrm. of phosphorus, or to 0·3088 mgrm. of phosphorus pentoxide. Whenever possible, it is advisable to determine the phosphorus equivalent of the standard alkali by carrying through the whole process on a substance of a similar nature to that under examination, having previously determined the phosphorus content of the standard substance by the gravimetric process. Alternatively, the carbonate-free sodium hydroxide is standardised against exactly 0·1N-acid and its phosphorus equivalent is calculated from the ratio 23NaOH : 1P.

In Neumann's modification[3] the precipitated ammonium phosphomolybdate is washed three times with 50 c.c. portions of ice-cold water, when the precipitate is assumed to have the composition $(NH_4)_3PO_4.12MoO_3.2HNO_3$.

[1] W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, New York, 567, 1929.

[2] It is essential that the acid and alkali should be exactly equivalent to each other.

[3] A. Neumann, *Zeit. physiol. Chem.*, 37, 129, 1902; 43, 35, 1904; J. P. Gregerson, *ib.*, 53, 453, 1907; I. Bang, *Biochem. Zeit.*, 32, 443, 1911; J. M. Krasser, *Zeit. Nahr. Genuss.*, 21, 198, 1911; A. E. Taylor and C. W. Miller, *Journ. Biol. Chem.*, 18, 215, 1914; H. S. H. Wardlaw, *Journ. Roy. Soc. N.S. Wales*, 48, 73, 1914.

After dissolving in excess of standard 0·5N alkali, the solution is boiled before titration, thus liberating ammonia from the ammonium salts produced in the neutralisation. The ratio NaOH : P now becomes 28 : 1; hence 1 c.c. of 0·5N-NaOH represents 0·554 mgrm. of phosphorus. Heubner and Jodidi [1] have shown that an empirical value of 0·565 to 0·57 agrees better with the experimental results than the calculated figure of 0·554.

For certain purposes a sufficiently close approximation to the amount of the precipitated ammonium phosphomolybdate can be obtained by measuring the volume of the precipitate collected in the graduated test tube of a centrifugal machine. [2]

In Emmerton's process [3] the washed ammonium phosphomolybdate is dissolved in ammonia and the solution reduced by, say, zinc and sulphuric acid, whereby the molybdenum trioxide, MoO_3, is converted to the green oxide, Mo_2O_3 or $Mo_{12}O_{19}$. [4] The solution is rapidly filtered from the undissolved zinc, if necessary, and titrated with potassium permanganate, when the green oxide is re-oxidised to $Mo\ O_3$. See page 451.

§ 330. The Volumetric Determination of Phosphorus— Uranium Process.

Uranium acetate or nitrate reacts with phosphates in aqueous solution forming uranium phosphate. When all the phosphorus has been transformed to uranium phosphate, any further addition of the uranium salt gives a solution which produces a reddish-brown coloration when brought in contact with a solution of potassium ferrocyanide. These facts are utilised in a volumetric process. The reaction takes place somewhat slowly in the cold and, in consequence, the titration is generally finished with hot solutions—about 90°. The reaction is supposed to be slower in the presence of acetates and hence the concentration of acetate in the solution should be kept as low as possible. [5] But even when uranium nitrate is used for the titration, there is a considerable amount of acetate present. The amount of acetate added as uranium acetate is but a small fraction of the whole. Consequently, it makes little difference whether uranium nitrate or acetate is used in the titration. [6] When the uranium solution is used for titrating calcium phosphates, e.g. bone ash, it

[1] W. Heubner, Biochem. Zeit., 64, 393, 1914; S. L. Jodidi, Journ. Amer. Chem. Soc., 37, 1708, 1915; S. L. Jodidi and E. H. Kellogg, Journ. Franklin Inst., 180, 349, 1915.

[2] V. Eggertz, Journ. prakt. Chem., (1), 79, 496, 1860; H. Wedding, Stahl Eisen, 7, 118, 1887; M. Ukena, ib., 7, 407, 1887; M. A. von Reis, ib., 9, 1025, 1889; 10, 1059, 1890; K. Bormann, Zeit. angew. Chem., 2, 638, 1889; C. Reinhardt, Chem. Ztg., 15, 410, 1891; H. F. von Jüptner, Oester. Zeit. Berg. Hütt., 43, 203, 1895; J. Ohly, Chem. News, 76, 200, 1897; H. Kleinmann, Biochem. Zeit., 99, 95, 1919.

[3] F. A. Emmerton, Trans. Amer. Inst. Min. Eng., 15, 93, 1886–7; O. F. von der Pfordten, Zeit. anal. Chem., 23, 432, 1884; A. A. Blair and J. E. Whitfield, Journ. Amer. Chem. Soc., 17, 747, 1895.

[4] Complete reduction to Mo_2O_3 is difficult, and the reduced oxide has, in consequence, been represented by different formulæ—Mo_2O_3 (Pfordten); $Mo_{12}O_{19}$ (Emmerton); $Mo_{24}O_{37}$ (Blair and Whitfield).

[5] A. Vozarik Zeit. physiol. Chem., 76, 433, 1912) says that the harmful concentration of free acetic acid begins at 0·36 per cent. with cochineal as indicator (footnote 6, p. 679), or at 0·6 per cent. with potassium ferrocyanide. With sodium, ammonium and magnesium acetates the harmful concentrations begin at 4, 2 and 0·75 per cent. respectively.

[6] F. Sutton, Chem. News, 1, 97, 122, 1860; C. Boedeker, Liebig's Ann., 117, 195, 1861; H. Neubauer, Archiv Wiss. Heilkunde, 4, 228, 1893; C. Pincus, Journ. prakt. Chem., (1), 76, 104, 1859; R. Arendt and W. Knop, ib., (1), 69, 401, 415, 1856; K. Broockmann, Rep. Anal. Chem., 1, 212, 1881; A. E. Haswell, ib., 2, 251, 1882 (the more uranium solution used, the higher becomes its relative value); C. Mohr, Zeit. anal. Chem., 19, 150, 1880; Chem. News, 45, 248, 1882; V. Edwards, ib., 59, 159, 1889; 73, 25, 1896; G. Guérin, Journ. de

is generally standardised against a solution of calcium phosphate of known strength.

The Standard Solutions.—Make a standard solution by dissolving 11·0958 grms. of pure dicalcium phosphate,[1] $Ca_2H_2(PO_4)_2.4H_2O$, in a slight excess of 10 per cent. nitric acid and neutralise the solution by the gradual addition of dilute ammonium hydroxide until a faint precipitate just remains. Redissolve the precipitate in a few drops of glacial acetic acid and dilute the solution to a litre.[2] 1 c.c. of this solution is equivalent to 0·01 grm. of normal calcium phosphate, $Ca_3(PO_4)_2$. Then dissolve 40 grms. of uranium nitrate or 35 grms. of uranium acetate in about 800 c.c. of water. Add a few drops of ammonia, when a slight turbidity will be produced; now add just enough acetic acid to clear the solution and make up to a litre.[3]

Standardisation of the Uranium Solution.—Take 25 c.c. of the standard calcium phosphate solution, add about 70 c.c. of water and 5 c.c. of ammonium acetate,[4] and run the uranium solution from a burette until a drop of the *clear* liquid[5] gives the first sign of a permanent reddish-brown coloration with a little powdered (solid) potassium ferrocyanide[6] on a white plate.[7] The solution

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Pharm., **5**, 143, 1882 ; *Rep. Anal. Chem.*, **3**, 157, 1883; O. Abesser, W. Jani, and M. Märcker, *Zeit. anal. Chem.*, **12**, 239, 1873; E. Kessel, *ib.*, 8, 164, 1869; C. Leconte, *Compt. rend.*, **29**, 55, 1849; W. Knop, *Chem. Centr.*, (2), **1**, 737, 769, 1856; A. Neumann, *ib.*, (1), 219, 1898; H. Rheineck, *Dingler's Journ.*, **200**, 383, 1870; A. Pavec, *Chem. Listy*, **1**, 313, 1875; W. Strecker and P. Schiffer, *Zeit. anal. Chem.*, **50**, 495, 1911; J. B. Coleman and J. D. Granger, *Journ. Soc. Chem. Ind.*, **11**, 328, 1892; R. B. Gibson and C. Estes, *Journ. Biol. Chem.*, **6**, 349, 1909; D. Crispo and R. W. Tuinzing, *Landw. Versuchs.-Stat.*, **88**, 131, 1916; J. W. Springer, *Zeit. angew. Chem.*, **32**, 192, 1919; F. Secligmann, *Chem. Ztg.*, **44**, 599, 1920; H. Kleinmann, *Biochem. Zeit.*, **99**, 19, 1919.

[1] J. A. Muller, *Bull. Soc. chim.*, (3), **25**, 1000, 1901; *Chem. News*, 85, 124, 1902.

[2] The strength of the solution may be confirmed, if there be any doubt of the purity of the calcium phosphate, by precipitating according to the molybdate process (page 675). If alkali phosphates are to be titrated, potassium phosphate is used. For this purpose, dissolve 9·5841 grms. of monopotassium phosphate—KH_2PO_4—in a litre of water; 1 c.c. of solution $\equiv 0·005$ grm. P_2O_5. The solution is standardised by evaporating a known volume of the solution to dryness in a platinum dish. Ignite the residue at the full heat of a Bunsen flame and weigh as KPO_3. Or the phosphorus in a known volume may be determined by the magnesium process (page 674). According to W. C. Dumes (*Chemist-Analyst*, 8, 12, 1914), pure silver phosphate, Ag_3PO_4, with the equivalent of 16·96 per cent. P_2O_5, is relatively easily prepared, non-hygroscopic and well suited for the preparation of standard solutions.

[3] The uranium salt should be free from uranium phosphate or ferric nitrate. Let the solution stand some days before it is standardised, otherwise the turbidity which sometimes develops, owing to the separation of uranium phosphate, may alter the strength of the solution. The less free acetic acid the better, since the solution is more sensitive in the absence of an excess of free acetic acid. See footnote 5, p. 678. The strength of the solution should be checked every three or four days.

[4] AMMONIUM ACETATE SOLUTION.—Dissolve 154 grms. ammonium acetate in water, add 100 c.c. of acetic acid (sp. gr. 1·04), and dilute the solution to a litre (2E). The object of the ammonium acetate is to prevent the formation of free nitric acid.

[5] If a little of the precipitated uranium phosphate be removed on the rod in making the spot test, a brown colour may be given with the ferrocyanide before the reaction is actually completed. L. Lematte and A. Delacroix (*Bull. Soc. chim. biol.*, 6, 521, 1924) add a large excess of sodium chloride to promote the precipitation of the uranium phosphate.

[6] Or a drop of a solution of 1·1 grms. of the same salt—potassium ferrocyanide—in 10 c.c. of water (E). J. C. Thomlinson (*Chem. News*, **114**, 239, 1916) condemns the use of ferrocyanide as an indicator. C. Malot (*Archiv Pharm.*, **2**, 246, 1887) uses, as indicator, an aqueous ammoniacal solution of cochineal just decolorised with nitric acid. Titrate with this solution as an internal indicator until a permanent green is obtained—E. Starkenstein, *Biochem. Zeit.*, **32**, 235, 1911; F. Repiton, *Mon. Sci.*, (4), **21**, (2), 753, 815, 1907; *Chem. Zentr.*, (2), 2078, 1907; (1), 295, 1908; E. J. Kocsis and L. Pollak, *Acta Lit. Sci. Univ. Hung. Fran. Joseph Sect. Chem. Min. Phys.*, **4**, 147, 1934.

[7] For the method of titration with a "spot" indicator, see page 344. If an excess of uranium solution be accidentally added, a known amount of the standard phosphate solution may be added, and the titration continued, allowance being made for the phosphate added.

must be well agitated after each addition of the uranium solution.[1] Then heat the solution to boiling,[2] when a drop will no longer react with the ferrocyanide. Add more uranium solution, drop by drop, until the brown colour with the ferrocyanide is again developed.[3] The result of this titration enables the strength of the uranium solution to be represented in terms of calcium phosphate.

Evaluation of Bone Ash.—Supposing that bone ash is to be analysed, dissolve 2·5 grms. of the dry (110°) sample in a minimum excess of hot, 10 per cent. nitric acid. Filter and wash the insoluble residue [4] well with hot, distilled water. Add ammonia to the filtrate and washings until a permanent precipitate is obtained. Redissolve the precipitate [5] in a few drops of glacial acetic acid and dilute to 250 c.c. Pipette out 25 c.c. of the solution, add about 70 c.c. of water and 5 c.c. of ammonium acetate solution. Then titrate with the uranium solution, as indicated above.

Calculation.—Suppose that 25 c.c. of standard solution contain the equivalent of 0·25 grm. of $Ca_3(PO_4)_2$ and n c.c. of the uranium solution are needed for the titration; obviously, 1 c.c. of the uranium solution represents $0·25/n$ grm. of $Ca_3(PO_4)_2$. If 25 c.c. of the bone ash solution, *i.e.* 0·25 grm. of bone ash, react with v c.c. of the uranium solution, then 100 grms. will react with $400v$ c.c. of the uranium solution, which represents $400v \times 0·25/n = 100v/n$ grms. of $Ca_3(PO_4)_2$.

Sodium Salicylate as Indicator.—Duparc and Rogovine [6] advocate the use of sodium salicylate as an internal indicator, based on the fact that an intense orange colour is formed when uranyl acetate comes into contact with an aqueous solution of sodium salicylate.

To 25 c.c. of the standard phosphate solution add 60 c.c. of water and 10 c.c. of a freshly prepared 10 per cent. solution of sodium salicylate. Titrate, as indicated above, with the uranium solution until, on allowing the precipitate to settle, the clear liquid has a distinct orange-yellow colour. Retain the titrated solution for comparison. Now take 25 c.c. of the bone ash solution, add 60 c.c. of water and 10 c.c. of the sodium salicylate solution and titrate in an exactly similar manner until the orange-yellow colour of the clear liquid is of the same intensity as in the previous titration. The method has been found to work well in routine analyses of bone ash.

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[1] In shaking, avoid making the solution froth, since a drop of uranium solution falling on the froth does not readily mix with the liquid underneath. A drop of alcohol will generally dispel the froth.

[2] If the solution be heated before the greater part of the phosphoric acid has combined with the uranium, some calcium phosphate may be precipitated (R. Fresenius, C. Neubauer and E. Luck, *Zeit. anal. Chem.*, **10**, 133, 1871; C. Schumann, *ib.*, **11**, 382, 1872).

[3] If the spot test gives a brown colour, add another four drops of the uranium solution. If the brown does not appear the moment the glass rod is removed, the first browning was not the end of the titration. This supplementary "four-drop test" should always be made.

[4] The insoluble earthy and sandy matters may be filtered off in a Gooch crucible, dried and weighed.

[5] If iron and alumina be present, phosphates of these elements will be precipitated and these remain insoluble in the acetic acid. In that case, filter the turbid solution. Titrate the filtrate as indicated in the text. Ignite and weigh the precipitate. If less than 0·01 grm. of the mixed phosphates be present, take half the weight as P_2O_5 and add the result to the P_2O_5 obtained by the titration. If over this amount of precipitate be present, the process is unreliable, or the P_2O_5 may be determined in the precipitate by the molybdate process (V. Edwards, *Chem. News*, **73**, 25, 71, 1896; G. H. Allibon, *ib.*, **73**, 47, 94, 1896). There is then no particular advantage in the volumetric process over, say, Woy's process. Other phosphates—*e.g.* cerium phosphate—may be precipitated if they be present—A. A. Damour and H. St C. Deville, *L'Institut*, **26**, 69, 1858; *Compt. rend.*, **59**, 272, 1864; J. Boussingault, *Ann. Chim. Phys.*, (4), **22**, 457, 1871.

[6] L. Duparc and E. Rogovine, *Helv. Chim. Acta*, **11**, 598, 1928.

Errors.—It will be noticed that a slight excess of uranium is needed to produce a coloration with potassium ferrocyanide, since enough uranium must be added not only to precipitate the phosphoric oxide, but also to colour the ferrocyanide. This excess must be allowed for by working under constant conditions and making a blank titration on a solution prepared as indicated above, for standardising the uranium, but excluding the phosphate, and always using the same volume of solution in the titration.

The most important sources of error in this titration with ferrocyanide as indicator are : (1) Mistaking a transient for a permanent brown—make sure, by means of the "four-drop test," that the brown tint is not an illusory end-point; (2) Error due to the removal of too small a drop to colour the ferrocyanide; (3) Error due to titrating too quickly and overreaching the end of the reaction; and (4) Error due to the retention of uranium solution by the froth and touching the ferrocyanide with this.

The analysis should be made in triplicate and no number should be accepted if it deviates appreciably from the others. It may be again emphasised that, while the agreement between the duplicates is a test of the accuracy of the work, it is not, as is sometimes supposed, an indication of the trustworthiness of the process. Some, expecting too much from this process, have given it up in disgust.

Owing to the almost invariable presence of appreciable amounts of alumina and iron, it may be advisable first to separate the phosphorus by means of ammonium magnesium citrate [1] before titration. If organic matter be present, it should be removed by a preliminary incineration, since organic matter interferes with the uranium reaction. Arsenic, if present, should be reduced by first passing a current of sulphur dioxide through the solution, boiling to remove the sulphur dioxide and precipitating the arsenic with hydrogen sulphide.[2]

PURCHASING BONE ASH.—According to the "English Form of the Hamburg Contract," bone ash is invoiced as follows :—

If the delivered bone ash contains BELOW 70 per cent. TRIBASIC PHOSPHATE OF LIME,[3] an allowance shall be made to the Buyers according to the following principle and scale :—

For Ash below 70 % for every   1 % less, 1½ % phosphate less to be invoiced.
     ,,   ,,   65 %   ,,   further 1 % ,,   2 %   ,,   ,,   ,,
     ,,   ,,   60 %   ,,   ,,   1 % ,,   3 %   ,,   ,,   ,,

For fractions, the allowance to be made on the same scale, for instance :—

69 % invoiced as 68½ %	65 % invoiced as 62½ %	61 % invoiced as 54½ %
68½ ,, ,, 67¾ ,,	64½ ,, ,, 61½ ,,	60½ ,, ,, 53½ ,,
68 ,, ,, 67 ,,	64 ,, ,, 60½ ,,	60 ,, ,, 52½ ,,
67½ ,, ,, 66¼ ,,	63½ ,, ,, 59½ ,,	59½ ,, ,, 51 ,,
67 ,, ,, 65½ ,,	63 ,, ,, 58½ ,,	59 ,, ,, 49½ ,,
66½ ,, ,, 64¾ ,,	62½ ,, ,, 57½ ,,	58½ ,, ,, 48 ,,
66 ,, ,, 64 ,,	62 ,, ,, 56½ ,,	58 ,, ,, 46½ ,,
65½ ,, ,, 63¼ ,,	61½ ,, ,, 55½ ,,	and so on

EXAMPLE.—Suppose 2·5 grms. of bone ash are taken for analysis. The solution is made up to 250 c.c., and 25 c.c. taken for a titration. Suppose $v = 13·3$ c.c. of the

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[1] H. Joulie, *Ann. Agronom.*, **11**, 97, 1885; *Chem. News*, **52**, 85, 1885; J. M. H. Munro, *ib.*, **52**, 86, 1885; L. Joulin, *ib.*, **27**, 228, 309, 314, 1873; C. Mène, *Compt. rend.*, **76**, 1419, 1873.

[2] RECOVERY OF URANIUM RESIDUES.—W. Jani, *Chem. Centr.*, 219, 1871; W. Knop, *ib.*, 161, 1865; F. Strohmer, *Zeit. anal. Chem.*, **17**, 84, 1878; A. Gawalovski, *ib.*, **15**, 292, 1876; E. Reichardt, *ib.*, 8, 116, 1869; **13**, 310, 1874.

[3] That is, normal calcium phosphate—$Ca_3(PO_4)_2$.

uranium solution are needed for the titration of this 25 c.c. of solution, and that $n = 20$ c.c. of the uranium solution are needed for titrating 25 c.c. of the standard phosphate. Then, from the above formula,

$$100 \times 13 \cdot 3/20 = 66 \cdot 5 \text{ per cent. } Ca_3(PO_4)_2.$$

If the phosphate be sold at 1s. 6d. per unit, a ton of the bone ash on the Hamburg scale is not invoiced at $66\frac{1}{2} \times 1\frac{1}{2} = £4$, 19s. 9d., but at $64\frac{3}{4} \times 1\frac{1}{2} = £4$, 17s. $1\frac{1}{2}$d. Naturally the colour, freedom from specks and working qualities of bone for pottery purposes are of more importance than "per cent. of normal phosphate."

§ 331. The Volumetric Determination of Phosphorus— Joulie's Magnesium Citrate Process.

Dissolve the substance under investigation in dilute hydrochloric acid or in a mixture of nitric and hydrochloric acids, if pyrites be present. If necessary, filter the solution.[1]

Separation of Phosphorus from Alumina and Iron as Magnesium Phosphate. —A portion of the clear solution, equivalent to 0·125 or 0·250 grm. of the phosphate, is pipetted into a beaker. Add 10 c.c. of magnesium citrate solution [2] and an excess of ammonia. The solution should be clear and only become turbid in a few seconds, especially after stirring.[3] Let the mixture stand under a bell-jar, to prevent loss of ammonia, overnight—that is, about 12–15 hours. Filter, first by decantation, and wash the precipitate with dilute ammonia (10 vols. water, 1 vol. ammonia). Four to six washings will suffice.[4]

Titration of the Magnesium Phosphate with Uranium Nitrate.—Dissolve the precipitate in a 10 per cent. solution of nitric acid. Allow the solution to run into the beaker in which the precipitation was made. Wash the filter-paper with acidulated water. Add dilute ammonia (1 : 10) until the solution is slightly turbid. Clear the turbidity with one or two drops of dilute nitric acid. Heat to boiling. Add 5 c.c. of sodium acetate solution [5] and titrate with the uranium acetate solution as described above.

§ 332. The Colorimetric Determination of Phosphorus.
(a) Knights' Process.

Knights' [6] colorimetric process for the determination of phosphorus is based upon the intensity of the yellow colour of the phosphomolybdate in acid

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[1] The removal of silica by evaporation is only necessary when the silicates are decomposed by the acid with the separation of gelatinous silica.

[2] JOULIE'S MAGNESIUM CITRATE SOLUTION.—Dissolve 20 grms. of pure magnesium carbonate or 10 grms. of pure magnesium oxide in 400 grms. of citric acid and 200 c.c. of distilled water. Add 500 c.c. of ammonia (sp. gr. 0·92), when the remainder of the citric acid dissolves; cool. If the solution be turbid, filter and make the clear solution up to a litre.

[3] An immediate turbidity shows that insufficient citrate is present to hold all the iron and alumina in solution. In that case, start again and use 20 c.c. of the citrate solution. It is not sufficient simply to add more of the citrate solution to the turbid solution, because the precipitate of the phosphates of iron and alumina, once formed, does not readily redissolve. W. Simmermacher (*Chem. Ztg.*, 37, 145, 1913) points out that if the magnesium citrate-citric acid solution be added slowly, a precipitate free from iron and silica is obtained, provided all the iron be in the form of citrate before the solution is made ammoniacal.

[4] The wash-water then gives no precipitate with sodium phosphate.

[5] SODIUM ACETATE SOLUTION.—A mixture of crystalline sodium acetate, 100 grms., and glacial acetic acid, 50 c.c., is made up to a litre with distilled water. The object of the sodium acetate solution is to prevent the development of free nitric or hydrochloric acid in the solution.

[6] J. West-Knights, *Analyst*, 5, 195, 1880.

solutions. This colour test is very sensitive, since 0·000025 grm. of P_2O_5 can be recognised in cold solutions, and 0·0000025 grm. in hot solutions (80°). As with colorimetric processes generally, the colour is influenced by the composition of the solution in which the determination is made.[1] The principal difficulty is due to the influence of traces of silica, which produce a potassium silicomolybdate with a yellow colour almost identical in tint with that of the potassium phosphomolybdate. It is therefore important to use reagents free from silica. The reagents must not be kept in glass vessels, owing to possible contamination by silica from the glass. The solutions should be kept in paraffin wax or ceresine bottles, or glass bottles coated internally with ceresine or paraffin wax. The absence of soluble silica in the reagents should be establised by a blank test.

A stock solution of phosphate is made by dissolving 0·1917 grm. of pure, freshly crystallised monopotassium[2] phosphate—KH_2PO_4—in silica-free water and diluting the solution to a litre. Preserve the solution in a ceresine or paraffin wax bottle. Each cubic centimetre corresponds with 0·0001 grm. P_2O_5.

Standard Solution.—Dilute 10 c.c. of the standard potassium phosphate to 80 c.c. with silica-free water. Add 10 c.c. of nitric acid (sp. gr. 1·07), and immediately add 8 c.c. of potassium molybdate solution.[3] Make the solution up to 100 c.c.[4]

Test Solution.—Acidify a convenient portion—say, 25 c.c.—of the solution under investigation with 5 c.c. of nitric acid (sp. gr. 1·07), add 4 c.c. of potassium molybdate solution and make the solution up to, say, 50 c.c.

The Comparison.—Make the two solutions up immediately and let them stand 20 minutes in order that the yellow tint of the phosphomolybdate may develop its maximum intensity. The intensities of the colours of the two solutions are now compared in a suitable colorimeter.[5] If the colour of the test solution be too strong for comparison, an aliquot portion is diluted as usual.

[1] P. E. Alessandri, *Pharm. Centr.*, **35**, 170, 1865; C. Lepierre, *Bull. Soc. chim.*, (3), **15**, 213, 1896; A. Jolles and F. Neurath, *Monats.*, **19**, 5, 1898; A. Jolles, *Arch. Hygiene*, **34**, 22, 1899; A. Pagnoul, *Ann. Agronom.*, **25**, 549, 1899; O. Schreiner, *Journ. Amer. Chem. Soc.*, **26**, 806, 1904; **25**, 1056, 1903; O. Schreiner and B. E. Brown, *ib.*, **26**, 1463, 1904; F. P. Veitch, *ib.*, **25**, 169, 1903; J. G. Smith, *ib.*, **26**, 897, 1904; T. E. Hewitt, *ib.*, **27**, 121, 1905; C. Estes, *ib.*, **31**, 247, 1909; F. P. Veitch, *Chem. News*, **89**, 73, 89, 101, 1904; I. Greenwald, *Journ. Biol. Chem.*, **21**, 29, 1915; C. E. Millar and F. A. Gangler, *Journ. Ind. Eng. Chem.*, **7**, 619, 1915; Z. Y. Tsen, *Acad. Sinica Inst. Chem. Mem.*, **4**, 1, 1931; G. Misson, *Bull. Soc. chim. Belg.*, **31**, 222, 1922.

[2] Sodium phosphate is difficult to deal with owing to efflorescence. J. A. Muller (*Bull. Soc. chim.*,(3),**25**, 1000, 1901) proposes the more stable microcosmic salt—$NaHNH_4PO_4.4H_2O$. The crystalline $Ca_3(HPO_4)_2.4H_2O$ is quite stable in dry air or over phosphoric anhydride in a desiccator. It is a valuable standardising agent.

[3] POTASSIUM MOLYBDATE SOLUTION.—Dissolve 8 grms. of the salt in 50 c.c. of water, and make the solution up to 100 c.c. with nitric acid (sp. gr. 1·2). According to Jolles and Neurath (*l.c.*), ammonium molybdate is liable to become turbid and is not so sensitive as sodium or potassium molybdate. The coloration develops its maximum intensity at 80° in a short time. The colour with potassium molybdate develops more quickly and is sharper and purer in tone than with sodium molybdate.

[4] N. Passerini (*Gazz. Chim. Ital.*, **41**, i, 182, 1911) recommends adding 2 c.c. of a cold saturated solution of gallic acid to the test glasses before the other solutions are added; J. Pouget and D. Chouchak (*Bull. Soc. chim.*, (4), **5**, 104, 1909; (4), **9**, 649, 1911) use strychnine sulphate with the phosphomolybdate.

[5] Nessler's glasses may be used in place of the colorimeter. One Nessler's glass is filled up to the 20 c.c. mark or the 50 c.c. mark with the test solution. At the same time, other Nessler's glasses are filled to the same volume with solutions containing different amounts of the standard phosphate solution and the molybdate solution. By comparing the tint of the standard with the tint of the unknown solution, the amount of phosphoric acid in the solution can be determined.

It is important to make sure that sufficient potassium molybdate is present to react with all the phosphate, by adding a further portion of the molybdate and diluting at the same time. The solution should contain 5 c.c. of nitric acid, and 4 c.c. of the potassium molybdate, per 50 c.c. of solution. Unless the standard and the test solutions have approximately the same amounts of these two reagents an appreciable error may be introduced. For smaller amounts of phosphorus, use a standard phosphate solution half the strength indicated above.[1]

Errors.—If the solution under investigation be turbid, it should be filtered through biscuit-ware [2] (page 717), evaporated to dryness and then taken up with water and again filtered. Organic matter, if present, may produce a coloured solution. In that case, the organic matter must be destroyed or a correction must be made. Veitch destroys organic matter by ignition with magnesium nitrate and subsequent evaporation with nitric acid. Large amounts of ammonium salts—nitrate and chloride—intensify the colour, and hence lead to high results. Aluminium sulphate—$Al_2(SO_4)_3$—gives a dark, more or less opaque solution which spoils the determination. If less than 1 part of iron per 20 million parts of the solution be present, no particular harm can be noticed, but if larger amounts be present, the colour is intensified, and the result is vitiated unless the amount of iron be known and an allowance made for its effect. If iron and alumina be present, therefore, the phosphorus should be separated as magnesium phosphate by Joulie's process before the phosphorus determination is made.[3] Calcium nitrate, barium chloride, potassium nitrate, separately and mixed together, give no appreciable error.

(b) Namias-Denigès Process.

A sensitive method, particularly suitable for determining traces of phosphorus in material of biological origin, is based on the fact that ammonium phosphomolybdate is reduced to "molybdenum blue" under conditions where the excess of ammonium molybdate, used in the process, is not reduced.

The blue oxide of molybdenum is generally regarded as Mo_3O_8, *i.e.* $MoO_2 \cdot 2MoO_3$, and it was characterised as such by Berlin in 1850; but Denigès maintains that it has the composition $MoO_2 \cdot 4MoO_3$.[4]

The production of "molybdenum blue" was used by Namias as far back as 1890 for the colorimetric determination of phosphorus though, in recent years, Denigès' name has become attached to the process.[5]

[1] For miscellaneous colorimetric processes, see H. Kleinmann, *Biochem. Zeit.*, **99**, 45, 1919; Y. Terada, *ib.*, **145**, 426, 1924; F. F. Tisdall, *Journ. Biol. Chem.*, **50**, 329, 1922; A. Grégoire, *Bull. Soc. chim. Belg.*, **29**, 253, 1920; C. V. Bordeianu, *Ann. Sci. Univ. Jassy*, **14**, 353, 1927; F. Alten, H. Weiland and H. Loofmann, *Zeit. Pflanz. Düng.*, **32A**, 33, 1933. See also footnote 3, page 685.

[2] If the nitric acid solutions be passed through ordinary filter-paper, there may be an error owing to the contamination of the solutions by phosphates and silica dissolved from the filter-paper.

[3] The magnesium phosphate is dissolved in nitric acid. The magnesia precipitate (page 210) may also be evaluated by determining the amount of phosphorus it contains colorimetrically and calculating the corresponding amount of magnesia. O. Schreiner and B. E. Brown, *Journ. Amer. Chem. Soc.*, **26**, 1463, 1904.

[4] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, London, **11**, 529, 1931; G. Denigès, *Compt. rend.*, **185**, 777, 1927.

[5] R. Namias, *Stahl Eisen*, **10**, 1060, 1890; E. Riegler, *Bull. Acad. Sci. Roumanie*, **2**, 272, 1914; P. N. van Eck, *Pharm. Weekb.*, **55**, 1037, 1918; G. Denigès, *Compt. rend.* **171**, 802, 1920; **185**, 777, 1927; *Compt. rend. Soc. biol.*, **84**, 875, 1921; *Mikrochem. Pregl Fest.*, 27, 1929; *Bull. Soc. pharm. Bordeaux*, 68, 1, 1930; *Chem. Zentr.*, (1), 2088, 1931; R. D. Bell

Details for the procedure, based on Truog and Meyer's work, are as follows :—

Standard Solution.—Dilute 10 c.c. of the stock phosphate solution (page 683) to 100 c.c. to give a diluted stock solution. Pipette out, say, 10 c.c. of the diluted stock solution into a 100 c.c. stoppered graduated cylinder. Dilute to 95 c.c. with silica-free distilled water, add 4 c.c. of acid ammonium molybdate solution [1] and shake thoroughly. Now add 6 drops of stannous chloride solution [2] and shake. Dilute to exactly 100 c.c. and again shake. This standard solution contains 1 grm. P_2O_5 per million c.c. of solution.

Test Solution.—A suitable volume of the solution under examination is, if necessary, made nearly neutral with acid or alkali according to circumstances. After dilution, the reagents are added to it, followed by final dilution to 100 c.c., exactly as in the preparation of the standard solution. In all cases the test solution must contain exactly 4 c.c. of the acid molybdate reagent and 6 drops of the stannous chloride solution per 100 c.c.

Comparison.— The test and standard solutions are compared in a colorimeter in the usual way. The two solutions must be made up immediately before use and the comparison should be made within 10 minutes after adding the stannous chloride solution, as thereafter the colour begins to fade. The addition of an extra drop of stannous chloride will restore the full colour for a further period of 10 minutes.[3] Magnesium, aluminium, calcium and man-

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and E. A. Doisy, *Journ. Biol. Chem.*, **44**, 55, 1920; A. P. Briggs, *ib.*, **53**, 13, 1922; **59**, 255, 1924; T. Kuttner and H. R. Cohen, *ib.*, **75**, 517, 1927; T. Kuttner and L. Lichtenstein, *ib.*, **86**, 671, 1930; D. Florentin, *Ann. Chim. anal.*, **3**, 295, 1921; L. Losana, *Giorn. Chim. Ind. Appl.*, **4**, 60, 1922; W. R. G. Atkins, *Journ. Agri. Sci.*, **14**, 192, 1924; M. von Wrangell, *Landw. Jahrb.*, **63**, 669, 1926; *Chem. Zentr.*, (2), 816, 1926; F. W. Parker and J. F. Fudge, *Soil Sci.*, **24**, 109, 1927; H. D. Chapman, *ib.*, **33**, 125, 1932; A. V. Levitzki, *Nauch. Agron. Zhur.*, **4**, 783, 1927; S. N. Rozanov, *Trans. Sci. Inst. Fertilisers, Moscow*, No. 55, 139, 1928; E. Truog and A. H. Meyer, *Ind. Eng. Chem. Anal. Ed.*, **1**, 136, 1929; H. D. Chapman, *ib.*, **3**, 282, 1931; R. J. Robinson and H. E. Wirth, *ib.*, **7**, 147, 1935; E. N. Isakov and V. A. Kazarineva, *Udobr. Urozhai*, **2**, 416, 1930; S. R. Zinzadze, *ib.*, **3**, 827, 1931; *Proc. Internat. Soc. Soil Sci.*, **6**, 95, 1931; *Ann. Agron.*, No. 3, 321, 1931; *Zeit. Pflanz. Düng.*, **16A**, 129, 1930; **23A**, 447, 1932; F. Alten, H. Weiland and H. Loofmann, *ib.*, **32A**, 33, 1933; L. Urbanek, *Mezög. Kutat*, **4**, 39, 1931; *Chem. Zentr.*, (1), 2643, 1931; E. Tschopp and E. Tschopp, *Helv. Chim. Acta*, **15**, 793, 1932; P. Urech, *Zeit. anal. Chem.*, **92**, 81, 1933; N. E. Prestov, *Journ. Chem. Ind. Russia*, **8**, Nos. 15–16, 22; No. 20, 15, 1931; W. R. G. Atkins and E. G. Wilson, *Biochem. Journ.*, **1223**, 1916; F. Pavelka and H. Morth, *Mikrochem.*, **16**, 239, 1934; N. Tatarinova and M. Makuchenko, *Chim. et Ind.*, **33**, 470, 1932; C. Zinzadze, *Ind. Eng. Chem. Anal. Ed.*, **7**, 227, 1935; H. L. Brose and E. B. Jones, *Nature*, **138**, 644, 1936; C. H. Fiske and Y. Subbarow, *Journ. Biol. Chem.*, **66**, 375, 1925; H. Etienne, *Bull. Soc. chim. Belg.*, **45**, 516, 1936.

[1] ACID AMMONIUM MOLYBDATE SOLUTION.—Dissolve 25 grms. of ammonium molybdate in 200 c.c. of distilled water at 60° and filter. Dilute 280 c.c. of sulphuric acid (sp. gr. 1·84), free from phosphorus and arsenic, to 800 c.c. When both solutions have cooled, add the ammonium molybdate solution, slowly and with constant shaking, to the solution of sulphuric acid. Again cool to room temperature and dilute to a litre.

[2] STANNOUS CHLORIDE SOLUTION.—Dissolve 25 grms. of stannous chloride, $SnCl_2.2H_2O$, in a litre of 10 per cent. (vol./vol.) hydrochloric acid. Filter if necessary. Store under a layer of mineral oil, to prevent atmospheric oxidation, in a bottle fitted with a syphon tube and burette tap from which the solution can be drawn off in drops. H. D. Chapman (*Soil Sci.*, **33**, 125, 1932) says that the solution oxidises slowly, even when covered with a layer of paraffin oil, but that it can be kept in narrow bottles for several months without serious deterioration.

[3] For the determination of small quantities of phosphorus by nephelometric methods, based on the insolubility of strychnine phosphomolybdate, see I. Pouget and D. Chouchak, *Bull. Soc. chim.*, (4), **5**, 104, 1909; **9**, 649, 1911; P. A. Kober and G. Egerer, *Journ. Amer. Chem. Soc.*, **37**, 2373, 1915; D. J. Matthews, *Journ. Marine Biol. Assoc. U.K.*, **11**, 122, 251, 1916–18; E. B. Meigs, *Journ. Biol. Chem.*, **36**, 335, 1918; H. Kleinmann, *Biochem. Zeit.*, **99**, 150, 1919; S. G. Clarke, *Analyst*, **56**, 518, 1931; E. Rautenberg, *Mikrochem.*, **10**, 467, 1932; F. Alten, H. Weiland and H. Loofmann, *Zeit. Pflanz. Düng.*, **32A**, 33, 1933.

ganese in considerable amounts are harmless, as is silica when not in excess of 700 parts per million. Ferric iron, if present, should be reduced to the ferrous state; organic matter may be removed by ignition with magnesium nitrate. Arsenates give a similar reaction to phosphates and must be removed by hydrogen sulphide. All reagents, apparatus, filter-paper and water should be tested for absence of phosphorus and arsenic. New glassware should be "weathered" by treatment for 24 hours with warm sulphuric-chromic acid mixture.

§ 333. The Simultaneous Determination of Phosphorus and Silica.

Silica, as indicated above, is the great enemy of the colorimetric process for phosphates, since it produces a yellow-coloured silicomolybdate which was used by Jolles and Neurath for the colorimetric determination of silica. Woodman and Cayvan [1] found that the colour of the silicomolybdate required from $1\frac{1}{2}$ to $2\frac{1}{2}$ hours to develop its maximum intensity. This gives a means of correcting the determination of phosphorus for the influence of silica, and also for determining the amount of silica in the phosphate solution. If nitric acid and ammonium molybdate be added to the solution as quickly as possible, a certain intensity of colour is developed by the silica. If, however, the ammonium molybdate be added an hour before adding the nitric acid, the intensity of the colour due to the silica is but half (0.49) as great as before. Phosphates give the same intensity under both conditions. Let x denote the amount of P_2O_5 present, and y the amount of silica present. The intensity of the colour produced by the silica is 1.25 times the intensity of the colour produced by the same amount of P_2O_5. Hence, $x + 1.25y$ will represent the joint effect of the silica and the phosphorus in terms of the phosphate standard, or

$$A = x + 1.25y \quad . \quad\quad . \quad\quad . \quad\quad . \quad\quad . \quad\quad (1)$$

The value of A is determined by the colorimetric process indicated above.

If, in preparing the test solution indicated above, the addition of the nitric acid be deferred for one hour, and the comparison made 20 minutes afterwards, the colour produced by the silica will be but half its former value. Hence, $x + \frac{1}{2}(1.25y)$ will represent the joint effect of the silica and the phosphorus in terms of the standard, or

$$B = x + \tfrac{1}{2}(1.25y) \quad . \quad\quad . \quad\quad . \quad\quad . \quad\quad (2)$$

Multiply this equation by 2, and subtract equation (1) from the result, and we get the value of x, that is,

$$\text{Amount of } P_2O_5 = 2B - A$$

Similarly, by subtracting one equation from the other, we get the value of y, or

$$\text{Amount of } SiO_2 = 1.6(A - B)$$

In illustration, suppose that we find the value A for P_2O_5 in the solution prepared by adding the ammonium molybdate and the nitric acid simultaneously to be 27, and the value of B for P_2O_5 in the solution when the nitric acid is added one hour after the ammonium molybdate to be 16. Obviously, from the above equations,

$$\text{Amount of } SiO_2 = 1.6(27 - 16) = 17.6$$
$$\text{Amount of } P_2O_5 = 2 \times 16 - 27 = 5$$

[1] A. G. Woodman and L. L. Cayvan, *Journ. Amer. Chem. Soc.*, **23**, 96, 1901; A. G. Woodman, *ib.*, **24**, 735, 1902; F. P. Veitch, *ib.*, **25**, 169, 1903; O. Schreiner, *ib.*, **25**, 1056, 1903; **26**, 808, 1904; A. T. Lincoln and P. Barker, *ib.*, **26**, 975, 1904; O. Schreiner and E. B. Brown, *ib.*, **26**, 1463, 1904.

When the proportion of phosphorus to silica is small, Lincoln and Barker recommend the addition of, say, 5 c.c. of the standard phosphate solution to the test solution and then conduct the process as indicated above. Due allowance is made for the phosphorus which has been added.

From what has been said above, it will be obvious that the colorimetric process may be used for the determination of small quantities of soluble silica when phosphorus is absent.[1]

§ 334. The Analysis of Bone China Bodies.

The following numbers represent the ultimate percentage composition of a typical fired body, and show the kind of mixture now under investigation :

SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	Na_2O	P_2O_5
38·0	16·0	1·2	1·0	22·0	2·5	1·5	18·0

With unfired bodies, free carbon, carbon dioxide and the loss on ignition may also have to be determined.[2] The amount of phosphoric oxide may or may not be sufficient to combine with all the alumina and ferric oxide. If the phosphoric oxide be in excess, lime and magnesia will be precipitated as phosphates along with the iron and aluminium phosphates.[3] It is therefore necessary to modify the scheme of analysis indicated for clays. Several processes have been devised for dealing with the problem.[4] The following

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[1] A. Jolles and F. Neurath, Zeit. angew. Chem., 11, 315, 1898; R. Salvadori and G. Pellini, Gazz. Chim. Ital., 30, i, 191, 1900; F. Dienert and F. Wandenbulcke, Compt. rend., 176, 1478, 1923; H. W. Swank and M. G. Mellon, Ind. Eng. Chem. Anal. Ed., 6, 348, 1934; I. P. Alimarin and V. S. Zverev, Trans. Inst. Econ. Minerals (U.S.S.R.), No. 63, 1934; O. Liebknecht, L. Gerb and E. Bauer, Zeit. angew. Chem., 44, 860, 1931. H. Hermann (Zeit. anal. Chem., 46, 318, 1907) recommends potassium tungstate in place of potassium molybdate as a qualitative test for colloidal (soluble) silica—page 765.

[2] For the minor constituents of bone ash, see W. L. Hill, H. L. Marshall and K. D. Jacob, Ind. Eng. Chem., 24, 1306, 1932.

[3] For the removal of phosphoric oxide in analysis and for the analysis of phosphated silicates, see C. C. Semple, Journ. Soc. Chem. Ind., 36, 933, 1917; G. Vortmann, Zeit. anal. Chem., 56, 465, 1917; J. S. Teletov and N. N. Andronikova, ib., 80, 351, 1930; Ukrain Chem. Journ., 4, 341, 1929; T. Millner and F. Kúnos, Zeit. anal. Chem., 92, 253, 1933; J. D Cauwood, J. H. Davidson and V. Dimbleby, Journ. Soc. Glass Tech., 13, 270T, 1929; J. Bougault and E. Cattelain, Journ. Pharm. Chim., (8), 14, 97, 1931; Compt. rend., 193, 1093, 1931; G. E. F. Lundell and J. I. Hoffman, Journ. Assoc. Off. Agric. Chem., 8, 184, 1924; B. Solaja, Zeit. anal. Chem., 80, 334, 1930.

[4] THE ACETATE PROCESS is based on the assumption that the iron and aluminium phosphates are precipitated from a slightly acetic acid solution containing ferric oxide, alumina, lime and phosphoric oxide by means of ammonium acetate. There are several modifications. The precipitate is contaminated with calcium phosphate—C. Glaser, Zeit. anal. Chem., 31, 383, 1892; W. Hess, Zeit. angew. Chem., 7, 679, 701, 1894; F. Wyatt, The Phosphates of America, New York, 150, 1892; R. T. Thomson, Journ. Soc. Chem. Ind., 5, 152, 1886; 15, 868, 1896; Chem. News, 54, 152, 1886. In the so-called CAUSTIC ALKALI PROCESS, the bases other than aluminium hydroxide are separated while the alumina is held in solution by the addition of an excess of caustic soda—L. Lasne, Bull. Soc. chim., (3), 15, 6, 118, 146, 1896; O. von Grüber, Zeit. anal. Chem., 30, 9, 1891; Chem. News, 63, 146, 1891. In the OXALATE PROCESS, the solution remaining after the separation of the silica is mixed with sufficient tartaric acid to prevent the precipitation of alumina, etc., when ammonia is added to the solution. The lime is then removed as calcium oxalate by the addition of ammonium oxalate. The filtrate is evaporated to dryness in a platinum dish and the organic matter destroyed by heat. The residue is taken up with hydrochloric acid, and the alumina, etc., separated as usual—L. Blum, Zeit. anal. Chem., 39, 152, 1900. H. Immendorff (Land. Vers. Stat., 34, 379, 1887) precipitates the lime as oxalate in a solution very slightly acidified with hydro-

method has been found to give good results in the routine analysis of bone china bodies. A great many of the details are carried out as described for clays and there is no need to repeat full particulars.

Loss on Ignition.—The loss on ignition is determined on a gram of the dry (110°) powdered sample in the usual way [1] (page 136).

Separation of the Silica.—Fuse up a further gram of the sample with sodium carbonate, cool, extract the cake with water and acidify with nitric acid instead of hydrochloric acid. Separate the silica as usual by two evaporations to dryness with an intervening filtration.[2] The residue left after evaporation of the separated silica to dryness with hydrofluoric and sulphuric acids may contain a trace of phosphorus pentoxide. Hence it is fused with a little sodium carbonate, the cake is decomposed with dilute nitric acid and the resulting solution added to the filtrate from the silica.

Separation of Phosphoric Oxide.—The phosphoric oxide is separated from the silica filtrate as ammonium phosphomolybdate by the alternative procedure given on page 674. Accordingly, for every 100 c.c. of filtrate add 15 c.c. of a 30 per cent. solution of ammonium nitrate. Add the acid ammonium molybdate solution [3] in the cold, then warm on a water bath but do not boil.[4] Finally stir well and stand overnight. Filter through a gravimetric paper of suitable size and wash the precipitate with acid ammonium nitrate solution [5] until free from molybdate.[6]

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chloric acid. See also footnote 5, page 587. In the SULPHATE PROCESS the lime is removed by precipitation as calcium sulphate in the presence of alcohol before the precipitation of aluminium and ferric phosphates by ammonia. E. Glaser, *Zeit. angew. Chem.*, 2, 636, 1889; R. Jones, *ib.*, 4, 3, 1891; J. H. Vogel, *ib.*, 4, 357, 1891; *Chem. Ztg.*, 15, 495, 1891; T. Meyer, *ib.*, 14, 1730, 1890; H. H. B. Shepherd, *Chem. News*, 63, 251, 1891; W. H. Krug and K. P. McElroy, *Journ. Amer. Chem. Soc.*, 17, 260, 1895; *Zeit. anal. Chem.*, 30, 206, 1891; T. M. Chatard, *Trans. Amer. Inst. Min. Eng.*, 21, 169, 1892–3; E. T. Teschemacher and J. D. Smith, *Chem. News*, 62, 84, 1890; N. Blattner and J. Brasseur, *ib.*, 76, 150, 1897; H. Herzog, *ib.*, 102, 25, 1910; *Journ. Ind. Eng. Chem.*, 1, 477, 1909; H. W. Wiley, *Principles and Practice of Agricultural Analysis*, Easton, Pa., 2, 224, 1908.

[1] For the volatilisation of phosphoric oxide during the calcination for loss on ignition, see E. Lautemann, *Liebig's Ann.*, 113, 240, 1860; S. Leavitt and J. A. Leclerc, *Journ. Amer. Chem. Soc.*, 30, 391, 617, 1908. A sample of cereals calcined at low redness gave 2·14 per cent. of ash and, at bright redness, 2·08 per cent. Another sample gave respectively 2·18 and 2·16 per cent. There was therefore no serious loss under the conditions of the experiment. G. Lechartier (*Compt. rend.*, 109, 727, 1890) found the loss of phosphorus and also of sulphur is not serious if the operation be properly done. For the loss of sulphur during the calcination, see also G. S. Fraps, *Journ. Amer. Chem. Soc.*, 23, 199, 1901; E. Fleurent and L. Levi, *Bull. Soc. chim.*, (4), 9, 379, 1911.

[2] The complete removal of sodium nitrate from the precipitated silica can be ascertained by mixing 0·5 c.c. of the washings with 1·3 c.c. of pure sulphuric acid in a porcelain crucible and adding 0·5 c.c. of a freshly prepared 0·02 per cent. solution of diphenylbenzidine in sulphuric acid. No blue colour should develop—E. A. Letts and F. W. Rea, *Journ. Chem. Soc.*, 105, 1157, 1913.

[3] As bone china bodies contain about 18 per cent. of P_2O_5 or 7·86 per cent. of phosphorus, 1 grm. of material will contain about 0·0786 grm. P. Thus, 0·0786/0·03 = 2·62 times the quantity of acid ammonium molybdate solution given on page 674 will be needed. Since it is advisable to have an excess of the reagent over the calculated quantity, dissolve 7 grms. of ammonium molybdate in 35 c.c. of water, add 3 drops of concentrated ammonia and pour the solution into 35 c.c. of concentrated nitric acid.

[4] When the precipitate has settled, the clear liquid should be tested with a little more of the molybdate reagent to make sure that enough has been added.

[5] ACID AMMONIUM NITRATE.—Dissolve 50 grms. of ammonium nitrate in water, add 40 c.c. of nitric acid (sp. gr. 1·42) and dilute to 1000 c.c.

[6] To a few c.c. of the washings add a few c.c. of ammonium sulphide. Stand for 5 minutes and then add concentrated hydrochloric acid, drop by drop. A brown to black precipitate indicates molybdenum. A trace of molybdenum may be shown by the appearance of a blue colour—"molybdenum blue."

The precipitate of ammonium phosphomolybdate is dissolved in ammonia [1] and the phosphoric oxide in the solution precipitated as ammonium magnesium phosphate (page 674).

Removal of Molybdenum.—The acid filtrate from the ammonium phosphomolybdate contains the excess of ammonium molybdate used for the precipitation and the molybdenum in it must be removed before the analysis is continued. The solution is therefore transferred to a capacious conical flask and concentrated ammonia added until a faint permanent precipitate is formed. Then add, say, 50 c.c. of 10 per cent. ammonium sulphide solution, shake well, stopper the flask and stand for 15 to 20 minutes. Transfer the flask to a fume cupboard and add concentrated hydrochloric acid, drop by drop, to the dark orange-coloured solution until acidic. Molybdenum is precipitated as the sulphide MoS_2.[2] Filter the bulky precipitate through a 15 cm. paper and wash it well with hot water. Again treat the filtrate with ammonia, ammonium sulphide (say 10 c.c.) and hydrochloric acid to ensure that the last traces of molybdenum have been precipitated.[3] The final filtrate, after the complete removal of molybdenum, is boiled to expel hydrogen sulphide, oxidised with a few c.c. of nitric acid and, if necessary, evaporated to about 250 c.c. From this point onwards the analysis is continued as with the filtrate from the second silica in a normal clay.[4] The alkalies are determined on a separate sample.

A typical analysis of a bone china body by the above procedure gave :—

SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	Na_2O	P_2O_5	Loss	Total
32·29	14·59	0·13	0·06	26·34	2·82	0·43	18·62	5·04	100·32

[1] Any residue, insoluble in ammonia, should be filtered off, washed and ignited in a platinum crucible. Fuse the residue with a little sodium carbonate, extract the cold cake with water, filter and wash. Acidify the filtrate with nitric acid, boil, make ammoniacal and add the solution to the ammoniacal solution of the ammonium phosphomolybdate. The insoluble residue on the paper, after the sodium carbonate fusion, is dissolved in nitric acid and the solution added to the filtrate and washings from the precipitate of ammonium phosphomolybdate.

[2] Z. Perkowski, *Przemysl Chem.*, **16**, 160, 1932; T. Millner and F. Kunos, *Zeit. anal. Chem* **90**, 161, 1932; A. Lassieur, *Ann. Chim. anal. Chim. appl.*, **16**, 197, 1934. For the co-precipitation of iron with molybdenum sulphide, see page 447.

[3] The filtrate sometimes develops a blue colour, owing to the formation of a trace of "molybdenum blue." If this persists in the final filtrate, boil to expel hydrogen sulphide, oxidise the solution with a few drops of nitric acid and again treat, as before, with a few c.c. of ammonium sulphide solution.

[4] For the determination of magnesium in the presence of phosphates, see J. I. Hoffman, *U.S. Bur. Stand. Journ. Research*, **9**, 487, 1932; F. Thompson, *Ind. Chemist*, **10**, 142, 1934; G. Glomaud, *Journ. Pharm. Chim.*, (8), **19**, 14, 1934.

CHAPTER XLII.

THE DETERMINATION OF SULPHUR.

There is little chance of discovering any exact method for the determination of sulphates by precipitation as barium sulphate, which shall at the same time be generally applicable and require no corrections, and yet not owe its accuracy to a compensation of errors; for the reason that some of the requisite conditions appear to be mutually incompatible.—J. JOHNSTON AND L. H. ADAMS.

§ 335. The Properties of Barium Sulphate.

SULPHUR compounds in clays and silicates are transformed into soluble sulphates by fusion with sodium carbonate under oxidising conditions. The acidified solution is treated with a soluble barium salt and insoluble barium sulphate is precipitated. This is washed, dried, ignited in the usual manner and weighed as $BaSO_4$. The analytical value of barium sulphate was recognised very early. Bergmann made use of it about 1750 and Vauquelin, Kirwan and Klaproth, Aiken, Berard, Berzelius and other prominent workers on the foundations of analytical chemistry studied its composition.[1] Until comparatively recently, many books on analysis gave students the impression that the weight of the barium sulphate indicated the amount of sulphur trioxide in a given sample with unerring precision. It has long been certain that the results, unless definite precautions be taken, can only be approximately correct and may indeed be untrustworthy. The method, in fact, is peculiarly sensitive to modifications in the conditions of the experiment. In 1871, Glover[2] quoted the following analyses of seven different samples of pyrites by three different professional analysts, A, B, C:—

Table LXIV.—Test Analysis for Sulphur in Pyrites.

Sample No.	Per cent. of sulphur.						
	1.	2.	3.	4.	5.	6.	7.
A . . .	38·80	40·90	39·60	39·30	41·60	38·20	39·70
B . . .	38·00	40·90	39·10	39·50	41·40	38·00	39·20
C . . .	40·20	42·70	41·10	40·70	43·50	40·00	41·10

In some cases the difference amounts to about 2 per cent. Since somewhat similar results may be met with, even to-day, it is necessary to examine the more important sources of error.

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[1] T. Bergmann, *De Analysi Aquarum*, Stockholm, 1778; L. N. Vauquelin, *Ann. Chim. Phys.*, (1), 50, 168, 1804; J. E. Berard, *ib.*, (1), 71, 69, 1809; J. J. Berzelius, *ib.*, (1), 78, 30, 1811; A. Aiken, *Nicholson's Journ.*, 22, 304, 1809; R. Kirwan and M. H. Klaproth, *Gehlen's Journ.*, 5, 515, 1808. [2] J. Glover, *Chem. News*, 23, 57, 1871.

It is generally stated that sulphuric acid will show one part of "barium" in between 80,000 and 250,000 parts of solution. According to Böttger,[1] 0·0000015 gram-molecule of potassium sulphate per litre will give a sensible turbidity with barium chloride in about 6 hours, and 0·0000039 gram-molecule of barium chloride per litre will give a sensible turbidity with potassium sulphate in about 2 hours.

1. *The Adsorption of Salts by the Precipitated Barium Sulphate.*—The ease with which salts and acids, themselves soluble in water, are carried down and the difficulty of subsequently removing these impurities are characteristic of precipitating barium sulphate. Berzelius,[2] for example, said in 1820: "The impurities are in a state of combination which cannot be broken up by an excess of acid." Turner[3] also long ago pointed out that barium sulphate has a tendency to carry down other salts during its precipitation. He said (1829): "The adhesion of potassium sulphate to the precipitate ensues even in a dilute solution; and it is not prevented by the presence of other salts, such as potassium nitrate, ammonium chloride, or ammonium nitrate. The quantity of adhering salt is variable, depending apparently as well on the relative quantity of the two salts, and the strength of the solution, as on the manner and extent of edulcoration. I have known it to increase the weight of the barium sulphate by 1 per cent."

A large number of observers[4] have placed similar facts on record. Salts of the alkalies and the alkaline earths,[5] silica, magnesium, cobalt, copper,

[1] F. Jackson, *Journ. Amer. Chem. Soc.*, 25, 992, 1903; W. Böttger, *Zeit. angew. Chem.*, 25, 1992, 1912.

[2] J. J. Berzelius, *Ann. Chim. Phys.*, (2), 14, 376, 1820.

[3] E. Turner, *Phil. Trans.*, 119, 295, 1829; H. Rose, *Pogg. Ann.*, 113, 627, 1861. See also J. J. Berzelius, *Jahresbericht*, 142, 1831, and a discussion between Berzelius and T. Thomson, *ib.*, 77, 1827; *Phil. Mag.*, (2), 4, 453, 1828; (2), 5, 221, 1829.

[4] R. Fresenius, *Zeit. anal. Chem.*, 8, 52, 1869; 9, 52, 1870; 19, 53, 1880; 16, 339, 1877; 30, 452, 1891; R. Fresenius and E. Hintz, *ib.*, 35, 170, 1896; G. Brügelmann, *ib.*, 16, 19, 1877; E. Hintz and H. Weber, *ib.*, 45, 31, 1906; H. Weber, *ib.*, 45, 714, 1906; G. Lunge, *ib.*, 19, 419, 1880; C. Meineke, *ib.*, 38, 210, 1899; T. O. Sloane, *Journ. Amer. Chem. Soc.*, 3, 37, 1881; C. W. Foulk, *ib.*, 18, 793, 1896; J. Johnston and L. H. Adams, *ib.*, 33, 829, 1911; L. Archbutt, *Journ. Soc. Chem. Ind.*, 9, 25, 1890; W. Smith, *ib.*, 1, 85, 1882; P. Jannasch, *Journ. prakt. Chem.*, (2), 40, 233, 1889; C. Diehl, *ib.*, (1), 79, 430, 1860; R. Silberberger, *Monats.*, 25, 220, 1904; A. Ziegeler, *Chem. Centr.*, (3), 12, 555, 1881; W. Ostwald, *Zeit. phys. Chem.*, 34, 495, 1900; G. Hulett, *ib.*, 37, 385, 1901; 47, 357, 1904; F. W. Küster and A. Thiel, *Zeit. anorg. Chem.*, 22, 424, 1900; G. Hulett and L. H. Duschak, *ib.*, 40, 196, 1904; O. N. Heidenreich, *ib.*, 20, 233, 1899; A. Fischer, *ib.*, 42, 408, 1904; A. Thiel, *ib.*, 36, 85, 1903; T. W. Richards, *ib.*, 1, 150, 187, 1892; *Proc. Amer. Acad.*, 26, 258, 1891; T. W. Richards and H. G. Parker, *ib.*, 31, 67, 1896; O. Herting, *Zeit. angew. Chem.*, 12, 274, 1899; *Chem. Ztg.*, 23, 768, 1899; E. Ruppin, *ib.*, 33, 17, 398, 1909; 34, 1201, 1910; J. F. Sacher, *ib.*, 33, 28, 1909; O. Folin, *Journ. Biol. Chem.*, 1, 131, 1905; E. F. Teschemacher and J. D. Smith, *Chem. News*, 24, 61, 66, 171, 1871; N. Glendinning and A. Edgar, *ib.*, 24, 140, 220, 1871; S. Wyrouboff, *Bull. Soc. chim.*, (3), 21, 1046, 1899; J. I. Phinney, *Amer. J. Science*, (3), 45, 468, 1891; W. S. Allen and H. B. Bishop, *Internat. Cong. App. Chem.*, 8, i, 33, 1912; H. B. Weiser, *Journ. Phys. Chem.*, 21, 314, 1917; D. Balareff, *Zeit. anorg. Chem.*, 167, 237, 1927; 168, 154, 1927; 169, 257, 1928; *Zeit. anal. Chem.*, 72, 303, 1928; L. de Brouckère, *Bull. Soc. chim. Belg.*, 39, 174, 1930; *Journ. Chim. phys.* 27, 543, 1930; H. G. Grimm and G. Wagner, *Zeit. phys. Chem.*, 132, 131, 1928.

[5] For alkali sulphates, see E. Turner, *Phil. Trans.*, 119, 295, 1829; R. Bunsen, *Zeit. anal. Chem.*, 10, 396, 1871; H. Rose, *Handbuch der analytischen Chemie*, Leipzig, 2, 368. 1871; W. A. Turner, *Amer. Journ. Sci.*, (4), 38, 41, 1914; F. L. Hahn and R. Keim, *Zeit. anorg. Chem.*, 206, 398, 1932; B. Težak, *Bull. Soc. chim. Roy. Yougoslav*, 3, 147, 1932. Potassium chloride and chlorate, H. Rose, *Pogg. Ann.*, 113, 627, 1861; Kretschy, *Zeit. anal. Chem.*, 10, 396, 1871; B. Schultze, *Wagner's Jahresber.*, 264, 1882. Alkali chlorates and nitrates, R. Fresenius, *Zeit. anal. Chem.*, 9, 52, 1870; T. S. Gladding, *Journ. Amer. Chem. Soc.*, 16, 398, 1894. Lithium salts, K. Diehl, *Liebig's Ann.*, 121, 98, 1862; J. N. Friend and W. N. Wheat, *Analyst*, 57, 559, 1932.

iron [1] and aluminium compounds,[2] etc.,[3] may be carried down [4] with the precipitate. In illustration, known quantities of barium chloride and sulphuric acid were mixed in the presence of the salts indicated in Table LXV.; the results were somewhat high under conditions where slightly low results would have been obtained in the absence of the contaminating salts.

Table LXV.—Effect of Foreign Salts on the Precipitation of Barium Sulphate.

$BaCl_2.2H_2O$, grm. taken.	Salt added, 5 grm.	$BaSO_4$ found.	Error.
0·5046	..	0·4814	0·0004
0·5020	KCl	0·4931	+ 0·0137
0·5013	NaCl	0·4849	+ 0·0061
0·5027	$KClO_3$	0·4907	+ 0·0107

Hence, some of the salt carried down with the precipitate is probably weighed with the barium sulphate.[5] Further experiments show that occlusion occurs in presence of all the common metallic salts and of sulphates soluble in water; and that the amount of this occlusion per gram-molecule is nearly the same for all the metals. Hence, *all barium sulphate precipitates have a complex composition owing to the presence of occluded salts, e.g.* sodium nitrate,[6] ammonium salts, sodium, potassium and ammonium chlorides, potassium and

[1] According to C. R. Gyzander (*Chem. News*, 93, 213, 1906), ferrous salts are not so liable to contaminate the precipitated barium sulphate as ferric salts; hence, before precipitating the barium salt in the presence of iron, some recommend the addition of a reducing agent such as hydroxylamine hydrochloride.

[2] E. A. Schneider, *Zeit. phys. Chem.*, 10, 425, 1895; H. J. M. Creighton, *Zeit. anorg. Chem.*, 63, 53, 1909; L. Moser and P. Kohn, *ib.*, 122, 299, 1922: A. Mitscherlich, *Journ. prakt. Chem.*, (1), 83, 455, 1861.

[3] For the adsorption of:—Barium nitrate and chloride, see E. Mitscherlich, *Pogg. Ann.*, 55, 209, 1842; E. Siegle, *Journ. prakt. Chem.*, (1), 69, 142, 1856; H. Rose, *Pogg. Ann.*, 113, 627, 1861; F. W. Mar, *Amer. Journ. Science*, (3), 41, 288, 1891; P. E. Browning, *ib.*, (3), 45, 403, 1893; J. I. Phinney, *ib.*, (3), 45, 468, 1893; T. W. Richards and H. G. Parker, *Zeit. anorg. Chem.*, 8, 413, 1895; Z. Karaoglanow, *Zeit. anal. Chem.*, 56, 225, 1917; F. G. Germuth, *Amer. Journ. Pharm.*, 99, 271, 1927. Chromium salts, L. W. Winkler, *Zeit. angew. Chem.*, 33, 287, 1920; M. N. Pavlov, *Ukraine Chem. Journ.*, 2, 353, 1926; E. A. Nikitina and A. V. Babajeva, *Trans. Inst. Pure Chem. Reag.*, 10, 20, 1931. Cerium salts, J. C. G. Marignac, *Arch. Science phys. nat.*, 8, 265, 1848; *Liebig's Ann.*, 68, 216, 1848. Uranium and thorium salts, L. A. Vasil'eva, *Uchen. Zapiski Kazan Gosud. Univ.*, 90, 15, 1930. Platinum salts, C. E. Claus, *Journ. prakt. Chem.*, (1), 85, 129, 1862; *Jahresbericht*, 323, 1861. Vanadium salts, H. Rose, *Handbuch der analytischen Chemie*, Leipzig, 2, 456, 1871. Zinc chloride, P. Jannasch and T. W. Richards, *Journ. prakt. Chem.*, (2), 39, 321, 1889; F. W. Küster and A. Thiel, *Zeit. anorg. Chem.*, 22, 424, 1900. Sulphuric acid, H. Rose, *Handbuch der analytischen Chemie*, Leipzig, 2, 455, 1871; F. L. Hahn and R. Keim, *Zeit. anorg. Chem.*, 206, 398, 1932. Phosphoric acid, T. Scheerer, *Journ. prakt. Chem.*, (1), 75, 113, 1858; J. Spiller, *Chem. News*, 10, 219, 1864; T. von Fellenberg, *Mitt. Lebensmittelunters Hyg.*, 6, 191, 1915; *Chem. Zentr.*, (2), 1262, 1915; L. W. Winkler, *Zeit. angew. Chem.*, 33, 287, 1920; I. Majdel, *Bull. Soc. chim. Roy. Yougoslav*, 1, 25, 1931. Organic acids, P. Jannasch and T. W. Richards, *Journ. prakt. Chem.*, (2), 39, 325, 1889; J. Spiller, *Journ. Chem. Soc.*, 10, 110, 1858; T. S. Gladding, *Journ. Amer. Chem. Soc.*, 16, 398, 1894; F. W. Küster and A. Thiel, *Zeit. anorg. Chem.*, 19, 97, 1899.

[4] Either by adsorption or mechanically or in chemical combination.

[5] Y. Kato and I. Noda, *Mem. Coll. Sci. Eng. Kyōtō*, 2, 217, 1910; E. T. Allen and J. Johnston, *Journ. Amer. Chem. Soc.*, 32, 588, 1910; *Journ. Ind. Eng. Chem.*, 2, 196, 1910; W. A. Turner, *Amer. Journ. Sci.*, (4), 38, 41, 1914.

[6] This forms caustic soda on strong ignition.

sodium sulphates. Potassium salts are more likely to be occluded than sodium salts. Magnesium sulphate is scarcely occluded at all, and the error from alkali and ammonium chlorides is very small, unless very small precipitates are in question, when this error becomes of increasing importance. In general, *the greater the concentration of the alkali salts in the mother liquid, the greater the amount of salt occluded by the precipitate.* For instance, Allen and Johnston found that 350 c.c. of a solution containing the equivalent of 2 grms. of barium sulphate and 2 c.c. of a 2 per cent. solution of hydrochloric acid, gave the following results in the presence of sodium chloride:

Sodium chloride . . . 0   5   10   20   30   50   70   100 grms.
Occluded salt in precipitate . 8·2 17·4 19·0 24·4 31·4 38·4 45·8 47·6 mgrms.

Barium chloride, the precipitating agent, may also be carried down with the precipitated barium sulphate—about 0·15 per cent. is present in slowly formed precipitates.[1] Some of this may be removed by washing with dilute nitric or acetic acid, but another source of error may affect the work when the precipitate is subjected to acid treatment—page 697.

It is not always practicable to dissolve the precipitated barium sulphate and reprecipitate, as is frequently possible with most precipitates affected in a similar way. Mitscherlich[2] suggested purifying the precipitate by dissolving it in concentrated sulphuric acid[3] and reprecipitating the barium sulphate by dilution with water. The precipitate[4] is dissolved in a platinum crucible or dish with 10–15 c.c. of concentrated sulphuric acid and the solution poured in a thin stream, with vigorous stirring, into 350 c.c. of water. The solution is heated to facilitate the filtering of the purified barium sulphate. The soluble salts to a great extent remain in solution. Examples of two successive extractions of two different precipitates may be quoted:

	I.	II.
First extraction . .	0·0101	0·0248 grm. sodium sulphate.
Second extraction . .	0·0008	0·0021 grm. sodium sulphate.

This process is by no means satisfactory, particularly where the original precipitate is contaminated with barium salts. However, according to Rose,[5] the alkali salts are removed so completely that the spectroscope can afterwards detect but the merest traces of them. Berzelius[6] tried digesting the precipitate with hydrochloric acid, but the results were not satisfactory and Rose says that this treatment is "useless." Mar[7] obtained better results by evaporating

[1] A. Mitscherlich, *Pogg. Ann.,* 55, 214, 1842; E. Siegle, *Journ. prakt. Chem.,* (1), 69, 142, 1856; C. W. Foulk, *Journ. Amer. Chem. Soc.,* 18, 793, 1896; W. A. Turner, *Amer. Journ. Science,* (4), 38, 41, 1914; B. Težak, *B* . *Soc. chim. Roy. Yougoslav,* 3, 147, 1932.

[2] A. Mitscherlich, *Journ. prakt. Chem.,* (1), 83, 456, 1861; W. G. Mixter, *Chem. News,* 27, 53, 1873; *Amer. J. Science,* (3), 4, 90, 1872; F. H. Storer and A. H. Pearson, *ib.,* (2), 48, 870, 1869; F. A. Gooch and D. U. Hill, *ib.,* (4), 35, 311, 1913; *Chem. News,* 109, 195, 1914; Z. Karaoglanow, *Zeit. anal. Chem.,* 56, 225, 1917. F. Stolba (*Dingler's Journ.,* 186, 43, 1863; *Chem. News,* 9, 133, 1864) proposed to purify the barium sulphate by washing it with solution of copper acetate followed by hot water, but this is also "useless"—R. Fresenius, *Zeit. anal. Chem.,* 9, 52, 1870; H. Rose, *Handbuch der analytischen Chemie,* Leipzig, 2, 455, 1871; Z. Karaoglanow, *l.c.;* G. McP. Smith, *Journ. Amer. Chem. Soc.,* 39, 1152, 1917.

[3] J. Nicklès, *Amer. J. Science,* (2), 39, 90, 1865; *Chem. News,* 11, 125, 1865.

[4] E. Ruppin (*Chem. Ztg.,* 33, 17, 398, 1909; 34, 1201, 1910) boils the precipitate four times in acidulated water. J. F. Sacher, *ib.,* 33, 218, 941, 1909; M. J. van't Kruys, *Chem. Weekblad,* 6, 735, 1909.

[5] H. Rose, *Handbuch der analytischen Chemie,* Leipzig, 2, 27, 1871.

[6] J. J. Berzelius, *Ann. Chim. Phys.,* (2), 14, 376, 1820; G. Brügelmann, *Zeit. anal. Chem.,* 16, 22, 1877; H. Rose, *Handbuch der analytischen Chemie,* Leipzig, 2, 455, 1871.

[7] F. W. Mar, *Chem. News,* 63, 256, 1891; *Amer. J. Science,* (3), 43, 521, 1892.

the sulphuric acid solution of the sulphate to dryness, washing the crystals so obtained with water on an asbestos pad in a Gooch crucible, followed by ignition and weighing. The removal of silica by digesting the barium sulphate with hydrofluoric acid requires care, because barium sulphate is decomposed by the treatment. Thus Sleeper [1] obtained the following numbers on weighing 2·1563 grms. of barium sulphate after each successive evaporation with hydrofluoric acid:

$$2·1457 \quad 2·1295 \quad 2·1224 \quad 2·1041 \quad 2·1022 \quad 2·0800 \quad 2·0549$$

The barium sulphate, after the digestion, should be treated with a drop of sulphuric acid. As a matter of fact, Sleeper observed no contamination of the precipitated barium sulphate with silica when the former was precipitated from artificial mixtures of a soluble sulphate with sodium silicate.

Barium sulphate is freed from many impurities by fusion with four or more times its weight of potassium carbonate, whereby the barium is completely converted to carbonate, which can be washed, dried and weighed as such or re-converted to sulphate. Scheele did not know about this fusion method for decomposing heavy spar, for he used charcoal or honey; Marggraf used potassium carbonate to decompose Bologna stone; and Wieghe recommended Marggraf's process, but since he used only one and a half equivalents of potassium carbonate to one equivalent of barium sulphate, the decomposition was never complete. Later, Stromeyer used the carbonate for the same purpose. Rose [2] first worked out the proper mass relations for complete decomposition. He found it necessary to use six or seven times the *equivalent* weight of potassium carbonate to ensure complete conversion of the barium sulphate to carbonate, and even this amount of sodium carbonate does not decompose the sulphate completely after one and a half hour's fusion. However, on account of the lower molecular weight of sodium carbonate, a quantity of either carbonate equal to four times the actual weight of the barium sulphate will suffice for the decomposition of the latter.

The important thing is to avoid the mutual precipitation of salts from the mother liquid with the barium sulphate. The barium chloride solution should not be added suddenly, but rather in drops, gradually, with constant stirring. In illustration, the two following experiments may be cited to show the difference in the weight of the precipitate obtained when the barium chloride is added suddenly and in drops—the theoretical amount of barium sulphate was 49·33 per cent.:

	I.	II.
In drops	49·23	49·30
Suddenly	50·03	49·90

These and other experiments show that *the rapid addition of the precipitant gives a more impure precipitate than when the precipitant is added slowly.*[3] Indeed,

[1] J. F. Sleeper, *Chem. News*, **69**, 63, 1894.

[2] H. Rose, *Pogg. Ann.*, **95**, 96, 284, 426, 1855; C. W. Scheele, *Sämmliche physische und chemische Werke*, **2**, 179, 1793; A. S. Marggraf, *Chemische Schriften*, Berlin, **2**, 135, 1767; O. G. Wiegleb, *Crell's Neueste Entdeckungen in der Chemie*, **2**, 14, 1781; F. Stromeyer, *Untersuchungen über der Mineralkörper und anderer damit verwandter Substanzen*, Göttingen, 1821.

[3] Z. Karaoglanow, *Zeit. anal. Chem.*, **57**, 77, 1918; D. Balareff, *Zeit. anorg. Chem.*, **123**, 69, 1922; K. P. Chatterjee, *ib.*, **121**, 128, 1922; A. G. Murray, *Journ. Amer. Pharm. Assoc.*, **13**, 424, 1924; J. M. Taylor (*Journ. Soc. Chem. Ind.*, **42**, 294T, 1923; F. L. Hahn and R. Otto, *Zeit. anorg. Chem.*, **126**, 257, 1923; I. M. Kolthoff and M. J. van Cittert, *Pharm. Weekb.*,

if the precipitate which has been formed suddenly be fused with sodium carbonate, and, when cold, leached with water, filtered and the filtrate treated with silver nitrate as described on page 746, a precipitate of silver chloride is obtained corresponding, in amount, with the excess in the preceding figures, calculated on the assumption that the excessive amount of barium sulphate is due to adsorbed barium chloride. This demonstrates the adsorption of barium chloride by the precipitate formed under the conditions stated. If the barium chloride be added slowly, the contamination of the precipitates with phosphates is also reduced to a minimum.[1]

If much hydrochloric acid be also present,[2] a greater excess of barium chloride is needed to precipitate a given amount of sulphuric acid; and conversely,[3] a greater excess of a soluble sulphate is needed to precipitate a given amount of barium chloride. Hence, *the risk of contamination of the precipitated sulphate with barium chloride is greater, the greater the amount of free hydrochloric acid present*[4]; *but, within certain limits, the greater the acidity of the solution, the less the amount of the salt occluded by the precipitated barium sulphate.* Allen and Johnston consider that the best results are obtained when the "sulphate" solution contains 20 to 30 c.c. of 5N-hydrochloric acid per 500 c.c.,[5] and the amount of "sulphuric acid" is such that 5 to 10 c.c. of normal barium chloride solution are needed for the precipitation. If barium is to be determined, the solution should contain about 0·5 per cent. hydrochloric acid before adding the precipitating agent, say ammonium sulphate (10 per cent. solution). A considerable excess of the latter is needed for complete precipitation.

60, 1177, 1923; *Zeit. anal. Chem.*, **63**, 392, 1923) recommends running the barium chloride and sulphate solutions slowly and simultaneously into boiling water, acidulated with hydrochloric acid.

[1] T. von Fellenberg, *Mitt. Lebensmittelunters Hyg.*, **6**, 191, 1915.

[2] G. Hulett and L. H. Duschak (*Zeit. anorg. Chem.*, **40**, 196, 1904) found that, on heating to 600° the barium sulphate precipitated by sulphuric acid from barium chloride solution, some hydrogen chloride was evolved and the moistened residue afterwards reacted alkaline. Hence they argued that the precipitated sulphate is really a mixture of $Ba{<}^{SO_4H}_{SO_4H}$, $Ba{<}^{Cl}_{SO_4H}$ and $^{Ba}_{Ba}{>}SO_4 {<}^{Cl}_{Cl}$ and that these substances, when heated, form barium sulphate or a basic sulphate or chloride and hydrogen chloride. N. A. Rudnev (*Uchen. Zapiski Kazan Gosud. Univ.*, **90**, 1054, 1930) says that the use of barium nitrate, or the presence of nitric acid, gives high results owing to the formation of $(BaNO_3)_2SO_4$. The error increases with increasing concentration of nitric acid, reaches a limit and then decreases.

[3] F. W. Mar (*Chem. News*, **63**, 256, 1891; *Amer. J. Science*, (3), **41**, 288, 1891; (3), **43**, 521, 1892) and P. E. Browning (*ib.*, (3), **45**, 399, 1893) state that if a sufficient excess of sulphuric acid be present, the precipitation of barium as sulphate is not affected by the presence of up to 10 per cent. by volume of hydrochloric acid, nitric acid or aqua regia. E. Murmann (*Oester. Chem. Ztg.*, **13**, 227, 1910) recommends a large excess of hydrochloric acid with a few drops of alcohol to facilitate the precipitation of the barium sulphate. J. L. Osborne (*Journ. Phys. Chem.*, **17**, 629, 1913) coagulates the precipitate by the addition of a concentrated solution of ammonium acetate.

[4] J. O. Roos, *Kungl. Teknis. Högs. Materialpruf.*, **34**, 1896–1906; M. Huybrechts, *Bull. Soc. chim. Belg.*, **24**, 177, 281, 1910.

[5] O. Folin (*Journ. Biochem.*, **1**, 131, 1906) prescribes, as safe limits, 1 to 4 c.c. of concentrated hydrochloric acid per 150 c.c. of solution. K. P. Chatterjee (*Zeit. anorg. Chem.*, **121**, 128, 1922) says that the concentration of hydrochloric acid should not be greater than 0·1 per cent. by volume of the solution. L. W. Winkler (*Zeit. angew. Chem.*, **33**, 59, 1920) and H. R. Jensen (*Analyst*, **53**, 136, 1928) report losses when barium sulphate is precipitated in 0·01 to 0·02N-solutions of hydrochloric acid.

Jannasch and Richards [1] attributed the retention of iron by the precipitate [2] to the formation of a double ferric barium sulphate, and add that, in a solution containing ferric chloride, "an accurate determination of sulphuric acid by direct precipitation with barium chloride is not practicable." Hence, in determining sulphur in, say, pyrites the iron should be first removed, as Lunge recommends, by precipitation with ammonia before precipitating the barium sulphate.[3] An insignificant trace of sulphur may be lost owing to adsorption by the ammonia precipitate, or by the separation of a basic ferric sulphate with the ammonia precipitate. According to Lunge,[4] this need not be feared if the solution, after treatment with a moderate excess of ammonia, be heated to about 60° or 70° (not over) for about 10 minutes. The solution should still smell strongly of ammonia. The precipitate is filtered off and the sulphate precipitated from the filtrate as described below. With the same object in view, Treadwell [5] recommends supersaturating the solution with ammonia in the cold and afterwards raising the temperature almost to boiling with constant stirring. The precipitate is filtered and washed until the washings give no turbidity with barium chloride after standing 5 minutes.[6]

In addition to the (i) *double salt hypothesis* of Jannasch and Richards, there is the (ii) *complex salt hypothesis*. Ostwald suggested an analogy between the heated solution containing iron sulphate and solutions containing chromium sulphate and this led Küster and Thiel to assume that the complex $Ba(FeSO_4)_4$ is precipitated with the barium sulphate. Richards objected to this view and rather favoured the formation of a basic complex, $Fe(SO_4)OH$. It has not yet been possible from the data available to decide what complex is present. Schneider considers that the double salt hypothesis is unsatisfactory and

[1] G. S. Fraps, *Amer. Chem. Journ.*, 27, 288, 1902; R. Fresenius, *Zeit. anal. Chem.*, 9, 52, 1870; P. Jannasch and T. W. Richards, *Journ. prakt. Chem.*, (2), 39, 321, 1889; 40, 233, 1889; C. B. Williams, *Journ. Amer. Chem. Soc.*, 24, 658, 1902; G. McP. Smith, *ib.*, 39, 1152, 1917; J. H. Graham, *Journ. Franklin Inst.*, 159, 441, 1905; V. M. Shlapin, *Uchen. Zapiski Kazan Gosud. Univ.*, 88, 461, 1928; E. Turner, *Phil. Trans.*, 119, 291, 1829; C. E. Claus, *Journ. prakt. Chem.*, (1), 85, 129, 1862.

[2] For the adsorption of ferric salts by barium sulphate, see E. Dittler, *Kolloid Zeit.*, 21, 27, 1917; L. de Brouckère, *Bull. Acad. Roy. Belg.*, (5), 13, 827, 1927; (5), 15, 170, 1928; *Bull. Soc. chim. Belg.*, 38, 409, 1929; A. Giacalone and F. Russo, *Gazz. Chim. Ital.*, 66, 631, 1936.

[3] M. Dennstedt and F. Hassler, *Zeit. angew. Chem.*, 16, 1233, 1903; G. Lunge and R. Stierlin, *ib.*, 18, 446, 1656, 1921, 1905; G. Lunge, *ib.*, 16, 1081, 1903; *Zeit. anal. Chem.*, 19, 414, 1880; *Journ. Amer. Chem. Soc.*, 17, 69, 1895; T. S. Gladding, *ib.*, 16, 398, 1894; 18, 446, 1896; N. J. Lane, *ib.*, 18, 682, 1896; G. von Knorre, *Chem. Ind.*, 28, 2, 1906; K. Jene, *Chem. Ztg.*, 29, 362, 1905; H. Mennicke, *ib.*, 29, 4951, 1905; B. N. Gottlieb, *ib.*, 29, 668, 1905; F. W. Küster and A. Thiel, *Zeit. anorg. Chem.*, 19, 97, 1898; E. Martin, *Mon. Sci.*, (5), 3, (ii), 686, 1913; (5), 4, (i), 866, 1914; C. Zay, *Stat. sperim. agrar. Ital.*, 49, 530, 1916; *Chem. Zentr.*, (1), 446, 1917. F. Johnson (*Chem. News*, 70, 212, 1894) recommends reducing the ferric to ferrous iron by boiling the solution with sodium hypophosphite before the precipitation. W. S. Allen and H. B. Bishop (*Eighth Inter. Cong. App. Chem.*, 1, i, 33, 1912; H. C. Moore, *Journ. Ind. Eng. Chem.*, 8, 26, 1916) reduce the iron with aluminium powder. E. J. Virgin (*Teknisk Tids.* (*Kemi*), 53, 1, 1923) uses hydroxylamine hydrochloride. H. Koelsch (*Chem. Ztg.*, 43, 117, 1919) says that the prior removal of iron has little effect on the purity of the precipitate. See also I. M. Kolthoff and M. J. van Cittert, *Pharm. Weekb.*, 60, 1177, 1923; Z. Karaoglanow, *Zeit. anal. Chem.*, 56, 561, 1917. D. P. Liebenberg and S. Leith (*Journ. S. African Chem. Inst.*, 14, 47, 1931) reduce the ferric iron with potassium iodide.

[4] G. Lunge, *Zeit. anorg. Chem.*, 19, 454, 1899; F. W. Küster and A. Thiel, *ib.*, 19, 97, 1899; 22, 424, 1900; O. Herting, *Zeit. angew. Chem.*, 12, 274, 1899; O. Herting, *Chem. Ztg.*, 23, 768, 1899; O. N. Heidenreich, *Zeit. anorg. Chem.*, 20, 233, 1900; C. R. Gyzander, *Chem. News*, 93, 213, 1906.

[5] F. P. Treadwell, *Kurzes Lehrbuch der analytischen Chemie*, Leipzig, 2, 385, 1911.

[6] In doubtful cases the precipitate should be ignited and fused with sodium carbonate and the aqueous extract of the mass tested to make sure that sulphates are absent.

argues for the (iii) *solid solution hypothesis*, in which it is assumed that ferric sulphate can dissolve in barium sulphate only up to a point of saturation. Kolthoff and Vogelenzang maintain that the simultaneous precipitation of other salts with barium sulphate can be caused by (i) conglomerate formation, (ii) solid solution, (iii) adsorption, (iv) mixed crystals, (v) mechanical inclusion, and (vi) chemical reaction.[1]

2. *The Solubility of Barium Sulphate.*—Barium sulphate is but sparingly soluble in water,[2] 100 c.c. of water at 18° dissolving 0·00023 grm. of barium sulphate, while 100 c.c. of water at 100° dissolve 0·00041 grm. The freshly precipitated sulphate is rather more soluble than the precipitate which has stood for some time in contact with the mother liquid.[3] Curiously enough, *a precipitate of barium sulphate which is filtered and washed immediately after precipitation is less easily freed from occluded salts by the washing, and therefore contains more occluded salts than one which has been left to stand some time,* say overnight. The difference is considerable when the amount of the salt in the solution is large. For instance, a solution containing the equivalent of 2 grms. of barium sulphate and 5 grms. of sodium sulphate gave a precipitate containing:

Occluded Na_2SO_4	22·6	19·0	17·4	14·0	12·2	10·4	8·2	7·6 mgrms.
Time standing	15 min.	3 hrs.	18 hrs.	2 days	4 days	48 days	150 days	210 days.

These experiments were made at 20°. Experiments at 100° showed that rather less salt is occluded than at the lower temperature.

The solubility of the barium sulphate is augmented by acids.[4] Thus, 100 c.c. of a solution containing hydrochloric acid dissolved the following amounts of barium sulphate:

HCl	.	.	1·82	3·65	7·29	grms.
$BaSO_4$	.	.	0·0067	0·0089	0·0101	grm.

[1] W. Ostwald, *Zeit. phys. Chem.*, **29**, 340, 1899; F. W. Küster and A. Thiel, *Zeit. anorg. Chem.*, **22**, 424, 1900; **25**, 319, 1900; T. W. Richards, *ib.*, **23**, 383, 1900; E. A. Schneider, *Zeit. phys. Chem.*, **10**, 425, 1892; I. M. Kolthoff and E. H. Vogelenzang, *Pharm. Weekb.*, **56**, 122, 1919.

[2] F. Crace-Calvert, *Chem. Gaz.*, **13**, 55, 1856; *Manchester Lit. and Phil. Soc. Mem.*, **14**, 85, 1857; *Journ. prakt. Chem.*, (1), **68**, 305, 1856; A. F. Holleman, *Zeit. phys. Chem.*, **12**, 125, 1893; F. Kohlrausch, *ib.*, **50**, 355, 1905; **64**, 129, 1908; G. A. Hulett, *ib.*, **37**, 385, 1901; W. Böttger, *ib.*, **46**, 521, 1903; **56**, 83, 1906; R. Fresenius and E. Hintz, *Zeit. anal. Chem.*, **35**, 170, 1896; R. Fresenius, *ib.*, **9**, 52, 1870; **30**, 455, 1891; Z. Karaoglanow, *ib.*, **56**, 225, 1917; F. W. Küster, *Zeit. anorg. Chem.*, **12**, 261, 1896; D. Balareff, *ib.*, **145**, 122, 1925; A. C. Melcher, *Journ. Amer. Chem. Soc.*, **32**, 50, 1910; E. W. Neuman, *ib.*, **55**, 879, 1933; F. Margueritte, *Compt. rend.*, **38**, 308, 1854; M. Lemarchands, *ib.*, **187**, 601, 1928; I. M. Kolthoff and E. H. Vogelenzang, *Pharm. Weekb.*, **56**, 122, 1919; F. Kohlrausch and F. Rose, *Ann. Phys. Chem.*, (2), **50**, 127, 1893.

[3] *Cf.* page 201. W. H. Wollaston, *Phil. Trans.*, **103**, 51, 1813; W. Ostwald, *Zeit. phys. Chem.*, **34**, 495, 1900; G. Hulett, *ib.*, **37**, 385, 1901; **47**, 357, 1904; P. P. von Weimarn, *Grundzüge der Dispersoidchemie*, Dresden, 119, 1911; E. G. Pierce, *Chem. Engineer*, **24**, 62, 1916; H. B. Weiser, *Journ. Phys. Chem.*, **21**, 314, 1917.

[4] G. S. Fraps, *Amer. Chem. Journ.*, **27**, 288, 1902; H. Rose, *Pogg. Ann.*, **95**, 108, 1855; R. Piria, *Il Cimento*, **5**, 257, 1847; E. Siegle, *Journ. prakt. Chem.*, (1), **69**, 142, 1856; W. Ostwald, *ib.*, (2), **29**, 49, 1884; O. L. Erdmann and M. Mittenzwey, *ib.*, (1), **75**, 214, 1858; E. C. Nicholson and D. S. Price, *Phil. Mag.*, (4), **11**, 169, 1856; H. M. Noad, *Journ. Chem. Soc.*, **9**, 15, 1856; W. Ostwald and W. Banthisch, *Journ. prakt. Chem.*, (2), **29**, 52, 1884; C. Gutkowsky, *Ber.*, **5**, 330, 1872; G. Lunge, *Journ. Soc. Chem. Ind.*, **4**, 32, 1885; E. T. Allen and J. Johnston, *Journ. Amer. Chem. Soc.*, **32**, 588, 1910; T. S. Gladding, *ib.*, **16**, 398, 1894; R. Fresenius, *Zeit. anal. Chem.*, **9**, 62, 1870; Z. Karaoglanow, *ib.*, **56**, 225, 487, 1917; I. M. Kolthoff and E. H. Vogelenzang, *Pharm. Weekb.*, **56**, 122, 1919; F. C. Calvert, *Chem. Gaz.*, **13**, 55, 1856; M. Lemarchands, *Compt. rend.*, **187**, 601, 1928.

and nitric acid:

HNO_3	.	. 3·15	6·31	12·61	31·52 grms.
$BaSO_4$	.	. 0·0070	0·0107	0·0170	0·0241 grm.

Calvert noticed that precipitated barium sulphate is "less soluble in hydrochloric than in nitric acid," but in either case the solubility is sufficient "to cause chemists to avoid use of an excess of these acids in delicate analyses." Hence, if much free hydrochloric or nitric acid is present in the solution under investigation, it should be removed by evaporation.[1] Dilute sulphuric acid lowers the solubility, but barium sulphate is fairly soluble in the concentrated acid. Thus, 100 parts of sulphuric acid, sp. gr. 1·81, dissolve 0·66 part of barium sulphate, and 100 parts of anhydrous sulphuric acid dissolve 15·50 parts.[2] Again, 100 c.c. of 40 per cent. hydrobromic acid dissolve 0·04 grm. of barium sulphate; and the same amount of 40 per cent. hydriodic acid, 0·0016 grm.[3] Hydrogen peroxide[4] and free chlorine[5] also increase the solubility of barium sulphate.

Alkali chlorides, barium nitrate and potassium chlorate do not appreciably affect the solubility of barium sulphate; but alkali and ammonium nitrates,[6] phosphates and salts of the organic acids, have a marked effect on the solubility.[7]

Some substances inhibit the precipitation of barium sulphate. Thus, chromium salts[8] may entirely prevent the precipitate forming; ferric salts[9] behave in an analogous way, but much more feebly; tartaric and racemic acids restrain precipitation slightly and alkali citrates very markedly.[10] Under special conditions nitric,[11] metaphosphoric[12] and metaboric acids[13]

[1] R. Fresenius, *Zeit. anal. Chem.*, 9, 52, 1870; T. W. Richards and H. G. Parker, *Zeit. anorg. Chem.*, 8, 420, 1895.

[2] H. Struve, *Zeit. anal. Chem.*, 9, 34, 1870; C. C. Selleck, *Pogg. Ann.*, 133, 137, 1868; J. Nicklès, *Amer. Journ. Sci.*, (2), 39, 90, 1865; Liès Bodart and E. Jacquemin, *Compt. rend.*, 46, 1206, 1858; E. Varenne and M. Pauleau, *ib.*, 93, 1016, 1881; T. Garside, *Chem. News*, 31, 245, 1875; O. Aschan, *Chem. Ztg.*, 37, 1117, 1913; F. Bergius, *Zeit. phys. Chem.*, 72, 338, 1910; P. P. von Weimarn, *ib.*, 76, 218, 1911; Z. Karaoglanow, *Zeit. anal. Chem.*, 56, 225, 1917; N. R. Trenner and H. A. Taylor, *Journ. Phys. Chem.*, 35, 1336, 1931.

[3] A. R. Haslam, *Chem. News*, 53, 87, 1886.

[4] A. Gawalovski, *Zeit. Oester. Apoth. Ver.*, 44, 258, 1900.

[5] O. L. Erdmann, *Journ. prakt. Chem.*, (1), 75, 214, 1858.

[6] M. Mittentzwey, *Journ. prakt. Chem.*, (1), 75, 214, 1858; R. Fresenius, *Zeit. anal. Chem.*, 9, 62, 1870; J. J. Berzelius, *Ann. Chim. Phys.*, 14, 374, 1820.

[7] For the influence of various salts on the solubility of barium sulphate, see also Z. Karaoglanow, *Zeit. anal. Chem.*, 56, 225, 417, 1917; 57, 77, 1918; 106, 129, 1936; *Zeit. physikal. Chem.*, A178, 143, 1937; E. W. Neuman, *Journ. Amer. Chem. Soc.*, 55, 879, 1933. Karaoglanow concludes that, in general, the solubility of barium sulphate in electrolytes depends upon the ions present. Barium and sulphate ions lower the solubility; calcium and chloride ions are neutral, while hydrogen, sodium, potassium, strontium, divalent lead, ferric iron and nitrate ions all increase the solubility.

[8] A. Recoura, *Ann. Chim. Phys.*, (7), 4, 494, 1895; W. R. Whitney, *Zeit. phys. Chem.*, 20, 40, 1896; Z. Karaoglanow, *Zeit. anal. Chem.*, 56, 417, 1917; L. W. Winkler, *Zeit. angew. Chem.*, 33, 287, 1920; M. N. Pavlov, *Ukraine Chem. Journ.*, 2, 353, 1926.

[9] R. Fresenius, *Zeit. anal. Chem.*, 19, 53, 1880; Z. Karaoglanow, *ib.*, 56, 417, 1917; G. Lunge, *ib.*, 19, 419, 1880; T. S. Gladding, *Journ. Amer. Chem. Soc.*, 16, 398, 1894; W. Ostwald, *Zeit. phys. Chem.*, 29, 340, 1899.

[10] J. Spiller, *Journ. Chem. Soc.*, 10, 110, 1858; *Chem. News*, 8, 280, 1863; 19, 166, 1869.

[11] E. Schöne, *Pogg. Ann.*, 112, 214, 1861.

[12] T. Scheerer, *Journ. prakt. Chem.*, (1), 75, 113, 1858. A. Weisler (*Zeit. anorg. Chem.*, 28, 198, 1901) said he had no difficulty in analysing barium metaphosphate, whereas Graham stated that the acid prevents the precipitation. According to D. W. Horn (*Amer. Chem. Journ.*, 27, 495, 1902), the reference to Graham is wrong, for T. Graham (*Phil. Trans.*, 123, 253, 1833; *Pogg. Ann.*, 32, 69, 1834) obtained precipitates which were too heavy. The statement, usually found in text-books, which Weisler attributed to Graham, is based on

interfere similarly. It is possible that soluble double salts or complexes are formed in some cases. It is generally considered advisable to avoid, whenever possible, precipitating barium sulphate in the presence of free mineral acids, alkali and ammonium nitrates.

The solubility of the precipitate is increased by the presence of thorium, ferric and aluminium salts, but not so much by magnesium salts. Thus,

Grams per litre . .	1	2·5	5	10	25	50	100
			Grams of barium sulphate dissolved per 100 c.c.				
Ferric chloride . .	0·0058	0·0072	0·0115	0·0123	0·0150	0·0160	0·0170
Aluminium chloride .	0·0033	0·0043	0·0060	0·0094	0·0116	0·0170	0·0175
Magnesium chloride .	0·0030	0·0030	0·0033	0·0033	0·0050	0·0050	0·0050

The presence of copper nitrate, too, gives low results owing to the solubility of barium sulphate in an aqueous solution of copper nitrate. Hence, adds Phillips,[1] the nitric acid should be replaced by hydrochloric acid by converting the copper nitrate to chloride. The same difficulty does not then occur.

3. *The Reduction of the Sulphate to Sulphide.*— When barium sulphate is ignited in the presence of filter-paper or organic matter, "an appreciable amount of barium sulphate may be reduced to sulphide and the amount so reduced may be twice as great in a covered crucible as when ignited in an open crucible." The precipitate should be moistened with sulphuric acid, followed by evaporation to dryness, and again ignited in order to transform the sulphide back to sulphate.[2] According to Richards,[3] if the crucible be kept at such a temperature that the paper chars before bursting into flame, no considerable reduction occurs then, or in the subsequent burning-out of the charred paper. If a Gooch crucible be used, Ripper[4] says that the results are inaccurate, because the adhesion of the barium sulphate to the asbestos prevents the proper washing of the precipitate. This statement is opposed to the work of Mar and Phinney, who recommend the use of Gooch's crucible. With care, and the use of a good thick pad of asbestos, the Gooch crucible does not give results less accurate than filter-paper.

4. *Losses by Volatilisation.*— Barium sulphate is not appreciably decomposed at temperatures likely to be obtained during the ignition over a Bunsen

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the experiments of T. Scheerer (*Journ. prakt. Chem.*, (1), **75**, 113, 1858; confirmed by J. Spiller, *Chem. News*, **10**, 219, 1864), which showed the difficulty of satisfactorily precipitating barium sulphate in the presence of metaphosphoric acid. In explanation, it is possible that Weisler converted the meta- into the ortho-acid before precipitation—Spiller (*l.c.*) found that orthophosphoric acid has no solvent influence. R. Maddrell (*Liebig's Ann.*, **61**, 53, 1847) mentions no difficulty in analysing barium dimetaphosphate by heating it with sulphuric acid, while H. Lüdert (*Zeit. anorg. Chem.*, **5**, 33, 1894) obtained rather unsatisfactory results with the hexametaphosphates. T. Fleitmann (*Pogg. Ann.*, **78**, 361, 1849) avoided the difficulty in analysing barium metaborates by digesting the finely ground salt with sodium carbonate.

[13] D. W. Horn, *Barium Sulphate in Gravimetric Analysis*, Baltimore, 52, 1900; *Amer. Chem. Journ.*, **27**, 495, 1902.

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[1] H. J. Phillips, *Chem. News*, **62**, 239, 1890. For thorium, see E. White, *Thorium and its Compounds*, London, 26, 1912; F. R. Balcar and G. Stegeman, *Journ. Phys. Chem.*, **32**, 1411, 1928.

[2] C. W. Marsh, *Journ. Anal. App. Chem.*, **3**, 164, 1889; *Chem. News*, **59**, 309, 1889; S. F. Acree, *Journ. Biol. Chem.*, **2**, 135, 1906; H. Pellet, *Ann. Chim. anal.*, **12**, 186, 318, 1907; P. Truchot, *ib.*, **12**, 267, 1907; Z. Karaoglanow, *Zeit. anal. Chem.*, **56**, 225, 1917; I. M. Kolthoff and E. H. Vogelenzang, *Pharm. Weekb.*, **56**, 122, 1919; H. Koelsch, *Chem. Ztg.*, **43**, 117, 1919.

[3] T. W. Richards and H. G. Parker, *Zeit. anorg. Chem.*, **8**, 417, 1895.

[4] M. Ripper, *Zeit. anorg. Chem.*, **2**, 36, 1892; F. W. Mar, *Chem. News*, **63**, 256, 1891; *Amer. J. Science*, (3), **43**, 525, 1890; J. J. Phinney, *ib.*, (3), **45**, 468, 1891.

burner. Doeltz and Mostowitsch[1] found that a sample of pure barium sulphate lost 9 per cent. in weight when heated between 10 and 20 minutes in a platinum crucible at 1580°. This temperature is, however, much higher than is obtained in ordinary ignition, and if barium sulphate should be so decomposed, the original amount of barium sulphate can be restored by moistening with sulphuric acid and recalcination for a short time. If, however, much silica be present. appreciable decomposition may occur at much lower temperatures. Allen and Johnston[2] say that, if the barium sulphate be precipitated from solutions containing alkali sulphates, it "always occludes a certain amount of 'free' sulphuric acid which is taken up as acid sulphate of the alkali metal." Alkali chlorides increase the amount of this impurity, and it is greater with solutions containing potassium than sodium sulphate. The "free" sulphuric acid[3] is lost by volatilisation during ignition, whereas under ideal conditions all the sulphuric acid should have been converted into barium sulphate (in the determination of sulphur). If ammonium salts are present, some ammonium sulphate is precipitated with the barium sulphate; and since all but a trace of the occluded ammonium sulphate is driven off during ignition, the total loss by volatilisation is the resultant of these two effects. For instance, by adding ammonium chloride to 350 c.c. of a solution containing 20 per cent. of hydrochloric acid and the equivalent of 2 grms. of barium sulphate, the following results were obtained:

Table LXVI. - Volatilisation Losses during Ignition of Barium Sulphate.

Ammonium chloride.	Loss in grms.		
	Due to ammonium sulphate.	Due to "free" sulphuric acid.	Total.
grm.			
0	..	..	0·0112
0	..	..	0·0111
5	0·0244	0·0039	0 0283
5	0·0244	0·0055	0·0299
10	0·0259	0·0113	0·0372
10	0·0259	0·0096	0·0355

Hence, ammonium salts and a large excess of free acid should be avoided in solutions where the sulphur is to be determined.

5. *Sulphur in the Glass of Beakers and Flasks.*—According to Bunge,[4] baryta water and lime water can act on glass and a thin layer of corresponding sulphate is often deposited on glass in which such solutions have been used.

[1] F. O. Doeltz and W. Mostowitsch, *Zeit. anorg. Chem.*, 54, 146, 1907; W. Mostowitsch, *Metallurgie*, 6, 450, 1909; W. Schütz, *ib.*, 8, 228, 1910; J. Boussingault, *Compt. rend.*, 64, 1159, 1867; *Zeit. anal. Chem.*, 7, 244, 1868; Z. Karaoglanow, *ib.*, 56, 225, 1917; R. Bunsen, *Liebig's Ann.*, 111, 262, 1859; S. Popov and E. W. Neuman, *Ind. Eng. Chem. Anal. Ed.*, 2, 45, 1930; E. G. Mahin and B. Kilian, *Proc. Indiana Acad. Sci.*, 36, 155, 1929; C. W. Marsh, *Journ. Anal. App. Chem.*, 3, 164, 1889.

[2] E. T. Allen and J. Johnston, *Journ. Amer. Chem. Soc.*, 32, 588, 1910; *Journ. Ind. Eng. Chem.*, 2, 196, 1910.

[3] It arises from the free acid in the original solution, and increases with it up to a certain point.

[4] C. Bunge, *Zeit. anal. Chem.*, 52, 15, 1913.

Glass made from Glauber's salt (sodium sulphate) usually contains sulphates. Hence there is the possibility of a slight error by the solvent action of reagents on the glass vessels used in the analysis.

§ 336. The Determination of Sulphates in Clays and Insoluble Silicates.

The Fusion.—It is first necessary to get the silicate into solution. A gram of the dry material [1] is fused in a platinum crucible with five to six times its weight of sodium carbonate. If iron pyrites be present, about 0·25 grm. of sodium nitrite [2] should also be intimately mixed with the contents of the crucible. The mixture is heated very slowly as described for the potassium pyrosulphate fusion (page 166).

Preventing Contamination with Sulphur from Flame Gases.—In order to protect the contents of the crucible from sulphur compounds derived from the flame gases, Hillebrand [3] fits the crucible into a hole in an asbestos board; and Cumming, into a vitreous silica plate. The hole should be large enough to expose from one-half to two-thirds of the crucible to the flame. The asbestos will not stand the temperature many times, but its life may be prolonged by placing over a larger hole a disc of stout platinum foil with a hole for the crucible in the centre. The board should be inclined at an angle, as illustrated in fig. 144, so as to deflect the products of combustion upwards and prevent their contact with the mouth of the crucible.[4]
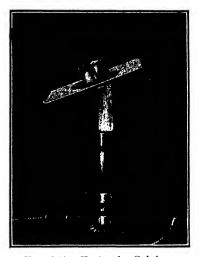
FIG. 144.—Fusion for Sulphur.

One of the many forms of blast lamp on the market burning methylated spirit may be used with advantage for the fusion. There is then no need to protect the crucible as just described. Barthel's lamps [5] are quite satisfactory.

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[1] If sulphur, chlorine and fluorine are to be determined, take 2 grms.

[2] Both nitrite and carbonate, and indeed all the reagents, should be tested to ensure the absence of sulphur compounds. (See footnote 6, page 706.)

[3] W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, 176, 196, 1900; A. C. Cumming, *Proc. Roy. Soc. Edin.*, 32, 17, 1912. The hole in the silica plate can be bored on a lathe with a copper tube fed with carborundum.

[4] CONTAMINATION WITH SULPHUR DURING IGNITION OVER GAS FLAMES.—See D. S. Price, *Journ. Chem. Soc.*, 17, 51, 1864; *Zeit. anal. Chem.*, 3, 483, 1864; A. Ieviņš, *ib.*, 102, 412, 1935; G. L. Ulex, *Zeit. Gesammt. Naturwiss.*, 36, 492, 1870; *Zeit. anal. Chem.*, 10, 246, 1871; J. W. Gunning, *ib.*, 7, 480, 1868; U. Collan, *ib.*, 32, 213, 1893; L. von Szathmary, *ib.*, 45, 600, 1906; R. Fresenius, *ib.*, 16, 339, 1877; A. Wagner, *ib.*, 20, 323, 1881; A. Lieben, *ib.*, 32, 214, 1893; *Mon. Sci.*, (4), 6, 683, 1892; *Monats.*, 13, 286, 1892; A. Vogel, *Ber.*, 2, 741, 1869; E. Přiwoznik, *ib.*, 25, 2200, 2676, 1892; G. Lunge, *Journ. prakt. Chem.*, (2), 40, 239, 1889; J. van Leeuwen, *Rec. Trav. Pays-Bas*, 11, 103, 1892; J. W. Gunning, *Chem. News*, 17, 161, 1868; R. Woy, *Zeit. öffent. Chem.*, 8, 389, 1902.

CONTAMINATION WITH SULPHUR DURING EVAPORATION OVER GAS FLAMES.—See O. Binder, *Chem. Ztg.*, 16, 254, 1892; E. von Meyer, *Journ. prakt. Chem.*, (2), 42, 267, 1892. On evaporating 2 litres of distilled water down to 50 c.c. in 6 hours on a water bath, Meyer found the water contaminated with sulphur equivalent to 0·0426 grm. of barium sulphate.

[5] G. Barthel, *Chem. Ztg.*, 14, 1443, 1890; 16, 1106, 1892; *Zeit. anal. Chem.*, 30, 596, 1891; 31, 67, 1892; *Ber.*, 25, 2646, 1892. Directions for use are supplied with the burner, which uses the principle of Bunsen's flame.

Fig. 145 illustrates one in use. These lamps may be obtained equivalent to one, two or four Bunsen burners. Electric crucible furnaces can also be used.

The Leaching of the Fused Cake.—When the fusion is completed and the crucible has cooled, the cake must be removed as described on page 144. The cake is digested in a porcelain basin with the washings from the crucible until
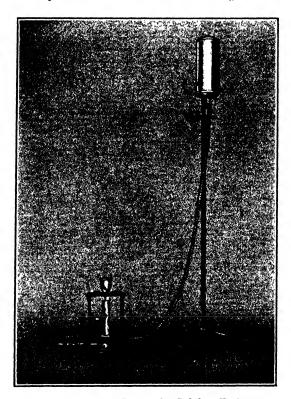
Fig. 145.—Spirit Burner for Sulphur Fusions.

it is completely disintegrated. Filter through a small filter-paper, say 9 cm., and wash with a dilute solution of sodium carbonate. If chromium be present, the solution will be yellowish. The filtrate contains the alkali sulphates, chlorides and silicates; and the sodium salts of chromic, vanadic, phosphoric, arsenic, molybdic and tungstic acids (if present). Barium carbonate, sodium zirconate and thoria, if present, remain undissolved on the filter-paper.[1] The filtrate is treated with barium chloride as described below.

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[1] For the subsequent treatment of the residue, see page 582. There is reason to suppose that a little sulphur sometimes remains behind with the residue—*e.g.*, with thoria—because in test experiments less sulphur is found than is known to be present—E. White, *Thorium and Its Compounds*, London, 26, 1912.

§ 337. The Determination of Sulphur as Barium Sulphate.

A drop of methyl orange is added to an aliquot portion (150- 250 c.c.) of the solution,[1] contained in a 500 c.c. beaker covered with a clock glass to prevent loss by spurting on neutralisation. Concentrated hydrochloric acid is now added, drop by drop, from a pipette, inserted through the lip of the beaker, until the solution is just acidic. An excess of hydrochloric acid is next added to the extent of 1 c.c. per 100 c.c. of solution.[2] Boil to expel carbon dioxide. Wash down the sides of the beaker and also the cover. Heat the dilute [3] solution to boiling and add, *gradually*,[4] say, 15 or 25 c.c. of a hot aqueous solution of barium chloride,[5] *with constant stirring*,[6] but avoid a *great* excess.[7] Boil for a few minutes.[8] If a drop of the supernatant liquid

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[1] If chlorine is to be determined, make the solution up to, say, 200 c.c., and set 100 c.c. aside for the chlorine determination (page 746). The volume of the solution should be such that not more than about 0·2 grm. of barium sulphate is precipitated from 100 c.c. of mother liquid. R. Bunsen (*Zeit. anal. Chem.*, 10, 396, 1871) recommends a dilution such that 100 c.c. gives about 0·1 grm. of barium sulphate.

[2] K. P. Chatterjee (*Zeit. anorg. Chem.*, 121, 128, 1922) says that the concentration of hydrochloric acid should not exceed 0·1 per cent. by volume. See also H. R. Jensen, *Analyst*, 53, 136, 1928.

[3] According to H. Rose (*Handbuch der analytischen Chemie*, Braunschweig, 1, 489, 1851) the precipitate is liable to run through the filter-paper if formed in concentrated solutions, and T. W. Richards and H. G. Parker (*Zeit. anorg. Chem.*, 8, 421, 1895) consider that the more dilute the solution the less the barium chloride is adsorbed by the precipitate. On the other hand, V. Njegovan and V. Marjanović (*Zeit. anal. Chem.*, 73, 271, 1928; 93, 353, 1933) say that by precipitating concentrated sulphate solutions with concentrated barium chloride, followed by dilution and heating for some time, a coarsely granular precipitate is formed which does not adsorb other salts from solution.

[4] Added from a burette or pipette with a capillary tip, so that about 4 minutes is needed for running in 20 c.c.—Z. Karaoglanow, *Zeit. anal. Chem.*, 57, 77, 1918; A. G. Murray, *Journ. Amer. Pharm. Assoc.*, 13, 424, 1924.

[5] BARIUM CHLORIDE SOLUTION.—Dissolve 122 grms. of barium chloride ($BaCl_2.2H_2O$) in 1000 c.c. of water (E). Here 1 c.c. corresponds with 0·104 grm. of $BaCl_2$. Note that commercial barium chloride sometimes contains sulphur compounds derived from the heavy spar used in making the chloride. The heavy spar is reduced to sulphide and some soluble unoxidised sulphur compound may be retained by the crystals of the chloride—J. Pattinson and J. T. Dunn, *Journ. Soc. Chem. Ind.*, 24, 10, 1905. Note also that rubber stoppers sometimes contaminate solutions with sulphur compounds derived from the vulcanising agent —antimony sulphide. It may also be added that barium chloride prepared as a by-product in the manufacture of hydrogen peroxide may contain an impurity which reduces potassium permanganate—L. Blum, *Zeit. anal. Chem.*, 29, 139, 1890.

[6] This point is of very great importance, particularly when much sulphate is to be precipitated. The object is to prevent, as far as possible, the mechanical inclusion of barium chloride with the precipitate.

[7] If a great excess of barium chloride is present, the precipitation is incomplete (Z. Karaoglanow, *Zeit. anal. Chem.*, 56, 417, 1917). According to J. J. Berzelius (*Lehrbuch der Chemie*, Dresden, 2, ii, 596, 1826), when solutions containing equivalent amounts of barium chloride and potassium sulphate are mixed, 2·25 per cent. of the barium remains in solution; and according to L. Joulin (*Ann. Chim. Phys.*, (4), 30, 274, 1873), when 1/5000N-sodium sulphate and barium chloride solutions are mixed, 1/27th of the salts remain undecomposed after 24 hours—precipitation is complete in about 4 days. H. Rose (*Handbuch der analytischen Chemie*, Leipzig, 2, 454, 1851) says that a certain excess of barium chloride hastens complete precipitation, and T. W. Richards and H. G. Parker (*Zeit. anorg. Chem.*, 8, 421, 1895) conclude that an excess of the barium salt diminishes the solubility of the precipitate while not increasing the amount of adsorbed barium chloride.

[8] When the precipitation occurs at the boiling temperature—both solutions hot—the precipitate is more granular, settles more quickly, filters better and washes easier than if the solutions be cold (page 85). H. Rose (*Handbuch der analytischen Chemie*, Leipzig, 2, 455, 1851) says that the precipitate formed in hot solutions is purer than in cooler solutions, and N. A. Menshutkin (*Analytical Chemistry*, London, 309, 1895) says that the precipitate is amorphous and runs through the filter-paper if formed in cold solution. Conversely, F. G. Germuth (*Amer. Journ. Pharm.*, 99, 271, 1927) advocates precipitation in the cold, both for concentrated and dilute solutions.

on a watch-glass gives a turbidity with a drop of barium chloride, add sufficient barium chloride, slowly, drop by drop, with constant stirring, to precipitate all the sulphate in solution.[1] If no turbidity occurs, let the solution stand 2 hours in a warm place, or, say, overnight.[2] Carefully decant the clear liquid through a (say, 7·5 cm.) filter-paper and wash four times by decantation with hot water,[3] containing 1 cubic centimetre of hydrochloric acid per litre.[4] Transfer the precipitate to the filter-paper and wash with hot water until a drop of the washings gives no turbidity with silver nitrate. The washing of the barium sulphate requires great care, because other salts are precipitated from the solution along with the barium sulphate. Ignite the wet precipitate in a platinum crucible. The paper is folded loosely over the precipitate to prevent spattering. The paper should be charred very gradually and the final temperature should not exceed dull redness. The crucible is then cooled and weighed. Evaporate with a few drops of hydrofluoric acid and a drop of sulphuric acid to expel any silica present.[5] Re-ignite in an inclined, uncovered crucible over the Bunsen flame [6] and again weigh. Any sulphides formed through the reducing action of the carbon of the filter-paper are soon re-oxidised and there is usually no need to add a drop of nitric acid and of sulphuric acid. If the washing has been properly done, the ignited barium sulphate will be a granular white powder; if otherwise, the powder may sinter to a more or less hard cake. The weight of the barium sulphate, multiplied by 0·13735, gives the corresponding amount of sulphur; the weight of the barium sulphate, multiplied by 0·34299, gives the corresponding amount of SO_3; and multiplied by 0·58324, the corresponding amount of calcium sulphate.

To illustrate the results which can be expected by this process, the following numbers represent the amounts of barium sulphate obtained in eight determinations with one-gram samples of the same clay:

0·0191; 0·0203; 0·0201; 0·0195; 0·0190; 0·0193; 0·0195; 0·0196 grm.

The mean is 0·0196; the maximum deviation, $\pm$0·0007 grm.—that is, $\pm$0·07 per cent. on the total clay.

§ 338. The Determination of Sulphur in Pyrites, Limestones and Coals.

The sulphur question is of importance in certain branches of the clay industries, not only on account of the defects produced in glazes by fuels with abnormal amounts of sulphur, but because the manufacture of some modern steels

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[1] J. Johnston and L. H. Adams (*Journ. Amer. Chem. Soc.*, 33, 829, 1911) recommend evaporation of the whole to dryness on a steam bath immediately after the precipitation. Extract the mass with hot water; filter through paper; wash until the washings are free from chlorides; ignite very carefully over a Bunsen burner to avoid reduction. The weight of the precipitate is corrected by dissolving an equivalent amount of pure potassium or sodium sulphate in a medium resembling the solution under analysis and determining the sulphate as just indicated. The difference between the calculated and found results is used as a correction factor for the weight of the precipitate obtained in the actual analysis. In that case it is supposed that results can be obtained within $\pm$0·05 per cent. of the total sulphur actually present in the solution.

[2] If a small amount of sulphur be present, the precipitate forms very slowly.

[3] Another beaker may be used for collecting the washings, to prevent having to re-filter *all* the liquid should the washings begin to run through turbid.

[4] It is well to test the runnings with a drop or two of sulphuric acid to make sure the barium chloride was in excess.

[5] If no silica is likely to be present, the ignition is conducted in a porcelain crucible.

[6] Not the blast, or SO_3 may be lost. See "4," page 699.

is influenced by the sulphur in the bricks, derived (1) by absorption from the fuel gases and (2) from the sulphates or pyrites in the clays themselves. The methods for the quantitative determination of sulphur in coal, clays and silicates may conveniently be grouped under four headings.[1] The selection of the process for any particular problem is to be decided by the number of determinations to be made, the object of the determinations and the nature of the samples under investigation.

The occlusion of iron by the precipitated barium sulphate was known to Berzelius,[2] who expressed the opinion (vide p. 696) that it is necessary to begin by removing the iron. Suggestions have been made to avoid the difficulty by— (i) Separating the iron and sulphur by fusion with some oxidising flux. Fresenius [3] fused pyrites with a mixture of potassium nitrate and alkali carbonates, extracted the cold mass with cold water, removed the nitric acid from the solution by evaporating with hydrochloric acid and then precipitated the sulphate. The method has been repeatedly tested and has come to be regarded as a criterion by which the accuracy of other methods can be judged.[4] It is considered, however, to be tedious and troublesome. The oxidising flux attacks the platinum crucible and the dissolved platinum may interfere with the iron determination,[5] and there is a danger of contamination from the sulphur in the coal gas when the fusion is done over a gas flame (page 701). (ii) Separating the iron as hydroxide, by means of aqueous ammonia, from the solution in which the sulphuric acid is to be determined—see Lunge's process, page 710. (iii) Reducing the iron in solution to the ferrous state before precipitating the barium sulphate.[6] The idea is that the ferrous iron will not be carried down by the precipitating barium sulphate. The concensus of opinion is that the reduction is ineffective and that additional complications arise from the presence of excess of the reducing agent—zinc, aluminium, magnesium or sodium amalgam. (iv) Retaining the iron in solution by the addition of organic acids before precipitation. This scheme was proposed by Jannasch and Richards,[7] and they tried formic, acetic and citric acids, but no particular success was obtained.

I. *Dry Fusion with Alkalies followed by Treatment with Oxidising Agents.*

Eschka's Method for Coal and Coke.—This process [8] depends upon the oxidation of the sulphur of the fuel by the oxygen of the air in the presence of

[1] L. Campredon, *Dosage du Soufre dans les Produits de la Sidérugie*, Paris, 1896; H. C. Moore, *Journ. Ind. Eng. Chem.*, 7, 634, 1915.

[2] J. J. Berzelius, *Ann. Chim. Phys.*, (2), 14, 376, 1820; D. W. Horn, *Amer. Chem. Journ.*, 27, 500, 1902.

[3] R. Fresenius, *Zeit. anal. Chem.*, 16, 339, 1877; 19, 53, 1880.

[4] G. Lunge, *Zeit. anal. Chem.*, 19, 419, 1880; P. Jannasch and T. W. Richards, *Journ. prakt. Chem.*, (2), 39, 333, 1889; G. Lunge (with Obregia), *ib.*, (2), 40, 241, 1889; *Zeit. angew. Chem.*, 2, 476, 1889; T. S. Gladding, *Journ. Amer. Chem. Soc.*, 16, 401, 1894; *Chem. News*, 70, 182, 1894; G. Lunge and E. Misslin, *Zeit. anorg. Chem.*, 21, 198, 1899.

[5] P. Jannasch and T. W. Richards, *Journ. prakt. Chem.*, (2), 39, 334, 1889.

[6] P. Jannasch and T. W. Richards, *Journ. prakt. Chem.*, (2), 39, 322, 1889; F. W. Küster and A. Thiel, *Zeit. anorg. Chem.*, 22, 424, 1900; O. N. Heidenreich, *ib.*, 20, 233, 1899; G. Lunge and J. Bebie, *ib.*, 21, 200, 1900; C. Meineke, *Zeit. anal. Chem.*, 38, 209, 351, 1899; W. S. Allen and H. B. Bishop, *Eighth Inter. Cong. App. Chem.*, 8, i, 33, 1912; H. C. Moore, *Journ. Ind. Eng. Chem.*, 8, 26, 1916.

[7] P. Jannasch and T. W. Richards, *Journ. prakt. Chem.*, (2), 39, 325, 1889; T. S. Gladding, *Journ. Amer. Chem. Soc.*, 16, 339, 1894. F. W. Küster and A. Thiel (*Zeit. anorg. Chem.*, 19, 101, 1899) tried oxalic and tartaric acids with fair success.

[8] A. Eschka, *Oester. Zeit. Berg. Hütt.*, 22, 111, 1874; *Zeit. anal. Chem.*, 13, 344, 1874; L. Blum, *ib.*, 27, 445, 1888; O. Herting, *Chem. Ztg.*, 23, 768, 1899; G. L. Heath, *Journ. Amer. Chem. Soc.*, 20, 630, 1898; 21, 1127, 1899; S. S. Sadtler, *ib.*, 27, 1188, 1905; F. U. R. Steh-

magnesia[1] and sodium carbonate[2] and on the transformation of the products of the oxidation into sulphates. Bromine water is now generally used for the oxidation. The sulphates are then precipitated by barium chloride in the usual way. The results are good and the process is in common use. Details of the operation are as follows:

One gram[3] of the powdered[4] sample is intimately mixed in a 30 c.c. platinum[5] crucible with 3 grms. of Eschka's mixture,[6] and about 2 grms. more of this mixture is spread as a layer over the contents of the crucible to form a kind of cover. The open crucible is placed slant-wise on a triangle and heated with a sulphur-free flame—page 702. The mixture must be heated very gradually to drive off the volatile matter without risk of losing sulphur. A small escape of sulphur dioxide can be detected by its smell. The heating should never be such as to blacken the covering layer of Eschka's mixture. In about half an hour the lower half of the crucible should be red-hot and the temperature is then raised until the whole crucible is red-hot. It is an advantage to stir the mixture occasionally with a stout platinum wire. When all the black particles have been burnt—a condition recognised by the grey colour of the mixture in the crucible changing to a yellow or yellowish-brown colour—the crucible and contents are allowed to cool.

Transfer the more or less pulverulent mixture to a 200 c.c. beaker and digest it for about 30 minutes with 75 c.c. of hot water. Filter the clear liquid into a 300 c.c. beaker and wash the residue twice by decantation; then transfer it to the filter-paper and wash it with water until the beaker contains about 200 c.c. of liquid. Add a slight excess of bromine water, about 4 c.c., and enough hydrochloric acid to make the solution slightly acid. Boil and precipitate the sulphates with barium chloride as described on page 703.[7]

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mann, *ib.*, **24**, 644, 1902; A. C. Langmuir, *ib.*, **22**, 99, 1900; C. W. Stoddart, *ib.*, **24**, 852, 1902; A. A. Blair, *Journ. Ind. Eng. Chem.*, **1**, 689, 1909; F. M. Stanton and A. C. Fieldner, *Tech. Paper U.S. Bur. Mines*, **8**, 7, 1912; I. C. Allen and I. W. Robertson, *ib.*, **26**, 3, 1912.

[1] W. C. Ebaugh and C. B. Sprague (*Journ. Amer. Chem. Soc.*, **29**, 1475, 1907; *Chem. News*, **96**, 240, 1907; L. Sznajder, *Chem. Ztg.*, **37**, 1107, 1913) use zinc oxide in place of magnesia; T. St Warunis (*Zeit. anal. Chem.*, **50**, 270, 1911; *Ber.*, **45**, 869, 1912), copper oxide; S. D. Hayes (*Amer. Chemist*, **5**, 271, 1875), lime and soda; C. Fahlberg and M. W. Iles (*Ber.*, **11**, 1187, 1878), caustic potash (and bromine water); J. Clark (*Journ. Soc. Chem. Ind.*, **4**, 329, 1885), soda and magnesia. W. F. K. Stock (*Chem. News*, **30**, 211, 1874), and F. C. Garrett and E. L. Lomax (*Journ. Soc. Chem. Ind.*, **24**, 1212, 1905), prefer calcium oxide to magnesia, because it is more easily obtained free from sulphur.

[2] F. Hundeshagen (*Chem. Ztg.*, **16**, 1070, 1892; *Chem. News*, **66**, 169, 1892) says that sodium carbonate is not so efficient as potassium carbonate in retaining sulphur. J. O. Handy (*Journ. Anal. App. Chem.*, **6**, 611, 1892) considers that Hundeshagen's statement is of no significance in practice; and this agrees with the general opinion of those who use the process.

[3] If 0·6867 grm. of the sample be taken, every 0·001 grm. of barium sulphate represents 0·02 per cent. of sulphur.

[4] Large grains do not burn readily. If the powder passes a 60's lawn, it is generally satisfactory.

[5] A porcelain crucible can be used in place of a platinum crucible, but the combustion is then rather slower—particularly with coke.

[6] ESCHKA'S MIXTURE.—Two parts of light calcined magnesia are intimately mixed with one part of anhydrous sodium carbonate. Calcined magnesia of commerce often contains sulphate. If the amount is considerable, it can be removed by boiling with sodium carbonate. A correction can be made for the sulphur in the sodium carbonate and magnesia by means of a blank experiment.

[7] R. Fresenius (*Zeit. anal. Chem.*, **13**, 346, 1874) remarks that the process gives the total sulphur. If calcium sulphate be present in the form of gypsum, the latter can be decomposed by first boiling the weighed sample with sodium carbonate, filtering and washing—F. C. Calvert, *Chem. News*, **24**, 76, 1871.

II. *Dry Fusion with Alkalies and Oxidising Agents.*

In these processes the sample is fused with sodium carbonate and potassium nitrate, or sodium nitrate (page 701), or ammonium nitrate,[1] and the residue taken up with water and evaporated with hydrochloric acid to expel the nitric acid before treatment with barium chloride. Fusion with sodium peroxide[2] offers many advantages; the chief disadvantage is the violence of the reaction with coal. To overcome this difficulty, Parr ignites the mixture in a closed bomb of about 30 c.c. capacity, as described below.

Parr's Process for Coal, Coke and Sulphide Ores.—One gram of *finely* powdered potassium perchlorate[3] is weighed out and transferred to the fusion cup of the bomb and to it is added 15 grms. of sodium peroxide.[4] The cover is placed on the cup and the contents *thoroughly* mixed by shaking. Then 0·5 grm. of the coal is added and the mixture again well shaken.

FIG. 146.—Parr's Bomb.

For anthracites, cokes and sulphide ores, 0·2 grm. of pure benzoic acid is added to the mixture of potassium chlorate and sodium peroxide and incorporated with it before the addition of the weighed quantity of the sample.

After ignition and cooling, the fusion cup is removed from the bomb and placed in a 300 c.c. beaker; 50 to 75 c.c. of water are added and the beaker covered with a clock glass. The mixture is heated until the charge has dissolved up, when the cup is removed and rinsed. The solution is just neutralised with hydrochloric acid (from 30 to 34 c.c. of acid of sp. gr. 1·16 will be needed) and then 1 c.c. of acid in excess is added.
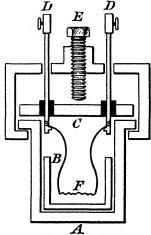
In one pattern of apparatus, the bomb, *A*, fig. 146, consists of a steel cylinder, 4 cms. internal depth, 3 cms. internal diameter, with walls 4 mm. thick, in which the fusion cup, *B*, rests. The bomb is closed by a cover plate,

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[1] S. F. and H. E. Peckham, *Journ. Soc. Chem. Ind.*, 16, 996, 1897; *Journ. Amer. Chem. Soc.*, 21, 772, 1899; W. Koch and F. W. Upson, *ib.*, 31, 1355, 1909; H. Schreiber, *ib.*, 32, 977, 1910; A. C. Langmuir, *ib.*, 22, 99, 1900; J. Lidow, *Journ. Russ. Phys. Chem. Soc.*, 31, 567, 1899; S. Aufrecht, *Pharm. Zeit.*, 41, 469, 1896; R. Dubois, *Bull. Assoc. chim. Belg.*, 15, 225, 1901; J. D. van Leeuwen, *Rec. Trav. chim.*, 11, 103, 1892; Z. Karaoglanow, *Zeit. anal. Chem.*, 56, 561, 1917; T. Gedeon, *Magyar Chem. Fol.*, 37, 71, 1931.

[2] S. W. Parr, *Journ. Amer. Chem. Soc.*, 22, 646, 1900; 30, 764, 1908; C. Sundstrom, *ib.*, 25, 184, 1903; J. D. Pennock and D. A. Morton, *ib.*, 25, 1265, 1903; C. Glaser, *ib.*, 20, 130, 1898; *Chem. Ztg.*, 21, 40, 1897; H. Koelsch, *ib.*, 40, 174, 1916; A. von Asbóth, *ib.*, 19, 2040, 1895; S. W. Parr, W. F. Wheeler and R. Berolzheimer, *Journ. Ind. Eng. Chem.*, 1, 689, 1909; H. C. Moore, *ib.*, 8, 26, 1916; F. H. Franklin, *ib.*, 5, 839, 1913; F. von Konek, *Zeit. angew. Chem.*, 16, 516, 1903; T. St Warunis, *Chem. Ztg.*, 34, 1285, 1910; E. Roe, *Chemist-Analyst*, 13, 4, 1915; D. P. Liebenberg and S. Leith, *Journ. S. African Chem. Inst.*, 14, 47, 1931; R. J. Rosser and F. N. Woodward, *Journ. Chem. Soc.*, 2357, 1932; H. Schillbach (*Zeit. angew. Chem.*, 16, 1080, 1903. W. Melzer, *Brennstoff Chemie*, 7, 313, 1926) uses barium peroxide.

[3] Potassium perchlorate has displaced the chlorate as an accelerator since, *inter alia*, the reaction with the perchlorate is not so violent—S. W. Parr, *Ind. Eng. Chem. Anal. Ed.*, 2, 10, 1930.

[4] If too little peroxide is used, the reaction is explosively violent; if too much, the combustion is incomplete. Imperfect mixing leads to explosive or incomplete combustion. The peroxide must be rapidly weighed and brushed from the watch-glass with a glass brush.

C, carrying two insulated pole pieces, *D*, *D*, which pass freely through holes cut in the cover itself. The cover plate is clamped in position by screw *E*, which engages the flanges on the cover and the bomb. The charge is "fired" by passing a current through a piece of iron fuse-wire, *F*, connecting the lower ends of the pole pieces.

III. *Oxidation by Heating the Substance in a Current of Air or Oxygen, under Ordinary or under Reduced Pressure.*

Combustion Process for Pyrites in Clays.—The determination of sulphur combined as pyrites can be effected in several different ways. The combustion process is as follows:—A hard glass tube, *A* (fig. 147)—length 40 cm.—is drawn out and bent at right angles [1] as shown at *B* in the diagram. One end of the glass tube is connected with a wash-bottle, *C*,[2] containing dilute potash solution (approximately 3N-KOH), and the other fitted with a pair of
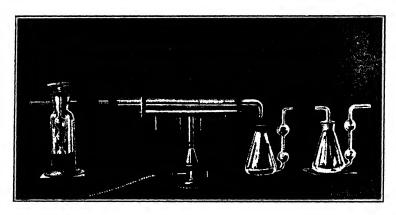
FIG. 147.—Determination of Sulphides.

Volhard's absorption tubes,[3] *D* and *E*, each containing about 50 c.c. of an aqueous solution of potash.[4] 10–20 grms. of the finely powdered and dried (110°) clay is spread in a thin layer on the bottom of a long porcelain boat, which, in turn, is placed in the combustion tube at *A*. The end *E* is connected with an aspirator and a current of air is drawn through the apparatus. The bubbles of gas should not pass through *C* more rapidly than admits of their being easily counted. The combustion tube is gradually heated to redness [5] in the vicinity of the boat containing the powder. Any deposit which forms

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[1] Uniform bends can be made in glass tubing of wider bores by first packing the tube well with powdered graphite and closing the ends of the tube with rubber bungs. The packed tube is then heated and bent as usual.

[2] S. Schiff, *Chem. Ztg.*, **14**, 233, 1890. Almost any other form will do quite well.

[3] J. Volhard, *Liebig's Ann.*, **176**, 282, 1875. The two shown in the diagram are modifications by R. Fresenius (*Zeit. anal. Chem.*, **14**, 333, 1875). M. Troilius' (M. Troilius, *Notes on the Chemistry of Iron*, New York, 37, 1886) or E. P. Perman's (*Chem. News*, **93**, 213, 1906), or any of the numerous other varieties of bulbs, can be used in place of Volhard's.

[4] POTASH SOLUTION: 16·8 grms. of potassium hydroxide freed from sulphates by alcohol are dissolved in water, 1 c.c. of bromine is added and the whole made up to 100 c.c.

[5] A Ramsay's attachment for an ordinary Bunsen burner is convenient for this purpose. W. Ramsay, *Chem. News*, **49**, 2, 1883.

in the tube in the vicinity of B should be driven forward by heating the tube with a spirit lamp, working the flame gradually from A to B. The sulphur dioxide formed is oxidised by the hypobromite in the absorption vessels to sulphuric acid.[1] At the end of the combustion—about 30 minutes—the absorption vessels are removed and the contents are washed into a beaker. Any sulphates remaining in the bent section of the tube AB are removed by drawing water up and down it by suction. The solution and washings are combined and hydrochloric acid added to neutralise the free potash and to decompose the potassium hypobromite. The whole is boiled and, if necessary, concentrated by evaporation. A hot aqueous solution of barium chloride is added and the barium sulphate determined as usual (page 703).

The clay is supposed to be free from calcium and magnesium carbonates; otherwise, calcium or magnesium sulphate may be formed, and the results will be correspondingly low. Water-soluble calcium and magnesium sulphates, however, may be determined before and after the combustion, and an allowance made for this disturbing reaction.

In some cases, say "*volatile sulphur*" *in fuels*, the combustion tube is packed towards the middle with about 5 cm. of platinised quartz or asbestos, instead of with copper oxide as in the combustion tube, page 640. The substance under investigation is placed in a boat on the opposite side of the platinised asbestos to the potash absorption bulbs. The tube is heated very gradually and a current of oxygen is passed through the system. The platinised asbestos ensures the oxidation of the sulphur dioxide and the potash solution absorbs the fumes of sulphuric anhydride.[2]

Combustion in the Bomb Calorimeter.[3]—The combustion of 0·7 to 1·0 grm. of the sample in a bomb containing 10 c.c. of water with oxygen under a pressure of 30 to 40 atmospheres [4] is said to give results "more accurate and rapidly than all other methods." The apparatus is rather expensive and hence is only used where a comparatively large number of determinations is made. There are several bomb calorimeters on the market and specific directions for manipulating the bomb are supplied with each instrument.

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[1] Hydrogen peroxide is sometimes used in place of bromine, and the sulphuric acid may be determined by titrating the standard potash solution used in D and E before and after the combustion. The clay is then supposed to be free from ammoniacal compounds, and the hydrogen peroxide from sulphur compounds. M. Fleischer, *Protocoll Sitz. Zentral-Moorkomm.*, **20**, 50, 1886; M. Berthelot and G. André, *Ann. Chim. Phys.*, (6), **25**, 302, 1892; M. van Bemmelen, *Lands. Vers. Stat.*, **37**, 284, 1890; P. Jannasch, *Chem. Ztg.*, **14**, 566, 1890; *Zeit. anorg. Chem.*, **6**, 303, 1894; *Journ. prakt. Chem.*, (2), **40**, 233, 1890; (2), **41**, 566, 1890; P. Jannasch, V. Wasowicz, K. Ashoff and T. Bicks, *ib.*, (2), **45**, 94, 1892; K. Zulkowsky, *Dingler's Journ.*, **241**, 52, 1881; L. P. Marchlewski, *Zeit. angew. Chem.*, **3**, 567, 1890; A. Sauer, *Zeit. anal. Chem.*, **12**, 32, 178, 1873; F. Muck, *ib.*, **14**, 16, 1875; W. Remmler, *ib.*, **33**, 75, 1894; O. Lindt, *ib.*, **4**, 370, 1865; O. Pettersson and A. Smitt, *ib.*, **32**, 385, 1893; W. G. Mixter, *Amer. J. Science*, (3), **4**, 90, 1871; M. Dittrich, *Zeit. anorg. Chem.*, **83**, 27, 1913; M. A. von Reis, *Stahl Eisen*, **14**, 963, 1894.

[2] C. F. Mabery, *Journ. Amer. Chem. Soc.*, **16**, 544, 1894; W. E. Barlow (with B. Tollens), *ib.*, **26**, 341, 1904; W. G. Mixter, *Amer. Chem. Journ.*, **2**, 396, 1880; G. Brügelmann, *Zeit. anal. Chem.*, **15**, 1, 1876; **16**, 1, 1877; A. Sauer, *ib.*, **12**, 32, 1873; C. M. Warren, *Proc. Amer. Acad.*, **6**, 472, 1871; I. Bay, *Compt. rend.*, **146**, 333, 1908; O. Dammer, *Zeit. angew. Chem.*, **22**, 440, 1909; O. Brunck, *ib.*, **18**, 1560, 1905; M. Holliger, *ib.*, **22**, 436, 1909; I. C. Allen and I. W. Robertson, *Tech. Paper U.S. Bur. Mines*, **26**, 8, 1912.

[3] I. C. Allen, W. A. Jacobs and G. A. Burrell, *Bull. U.S. Bur. Mines*, **19**, 8, 1911; I. C. Allen, *Min. Scient. Press*, **81**, 569, 1900; R. Arnold, R. Anderson and I. C. Allen, *Bull. U.S. Geol. Sur.*, **398**, 265, 1910; I. C. Allen and I. W. Robertson, *Tech. Paper U.S. Bur. Mines*, **26**, 10, 1912; G. A. Filliti, *Bull. Soc. chim.*, (4), **21**, 338, 1899; N. W. Lord, *Prof. Paper U.S. Geol. Sur.*, **48**, 174, 1906; D. Lohmann, *Chem. Ztg.*, **35**, 1119, 1911.

[4] If a lower pressure is used, there is a risk of incomplete combustion of the sulphur.

The treatment of the residue in the bomb is similar to that indicated above when dealing with Parr's process.[1]

IV. *Wet Treatment with Oxidising Agents under Ordinary or under High Pressures.*

The sample may be treated with various oxidising agents—aqua regia,[2] potassium dichromate and fuming hydrochloric acid,[3] hydrogen peroxide,[4] nitric acid and potassium nitrate[5] or nitric acid under pressure.[6] These methods are usually less convenient than the dry fusion processes.

Lunge's Wet Process[7] *for Pyrites.*—Warm 0·5 grm. of the given pyrites with about 100 c.c. of a mixture of 3 vols. of nitric acid (sp. gr. 1·4) and 1 vol. of concentrated hydrochloric acid, with occasional stirring, taking care to avoid loss by spurting. If free sulphur should separate,[8] add cautiously a little potassium chlorate in order to oxidise the sulphur to sulphuric acid. Evaporate the solution to dryness on a water bath and repeat the evaporation with 5 c.c. of concentrated hydrochloric acid until nitrous fumes cease to be evolved. Add 1 c.c. concentrated hydrochloric acid to the residue and, in a few minutes, 100 c.c. of hot water. Filter and wash with hot water.[9] Treat the combined filtrate and washings with a moderate excess of ammonia; heat the solution to 60° or 70° for 10 to 15 minutes. The solution should then smell strongly of ammonia. Filter and wash until the washings give no turbidity with barium chloride after standing for a few minutes.[10] The combined filtrates

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[1] If the bomb has a lead washer, the washings from the bomb are boiled for about 10 minutes with a 5 per cent. solution of sodium carbonate and then filtered. This treatment decomposes any lead sulphate which may be formed.

[2] E. Martin, *Min. Sci.*, (5), **3**, i, 686, 1913; (5), **4**, ii, 866, 1914; C. Zay, *Stat. sperim. agrar. Ital.*, **49**, 530, 1916; *Chem. Zentr.*, (1), 446, 1917; T. J. I. Craig, *Chem. News*, **115**, 253, 265, 1917; Z. Karaoglanow, *Zeit. anal. Chem.*, **56**, 561, 1917; D. P. Liebenberg and S. Leith, *Journ. S. African Inst. Chem.*, **14**, 47, 1931; H. A. J. Pieters and M. J. Mannens, *Chem. Weekb.*, **29**, 261, 1932; L. M. Iol'son, *Zavodskaya Lab.*, **3**, 116, 1934.

[3] K. Charitschkoff, *Petroleum Zeit.*, **2**, 714, 1907.

[4] E. V. Lecocq and H. Vandervoort, *Bull. Soc. chim. Belg.*, **16**, 181, 1902.

[5] F. W. Gill and H. S. Grindley, *Journ. Amer. Chem. Soc.*, **31**, 52, 1909; A. Goetzl, *Zeit. angew. Chem.*, **18**, 1528, 1905; F. C. Calvert, *Chem. News*, **24**, 76, 1871.

[6] L. Carius, *Liebig's Ann.*, **136**, 129, 1865; *Zeit. anal. Chem.*, **4**, 451, 1865; G. Anelli, *Rass. Min. Met. Chim.*, **34**, 1, 1911; R. Höland, *Chem. Ztg.*, **17**, 99, 130, 1893. For nitric acid and bromine, see G. Lunge, *Journ. Amer. Chem. Soc.*, **17**, 397, 1895; T. S. Gladding, *ib.*, **16**, 398, 1894; *Chem. News*, **70**, 181, 1894; T. J. I. Craig, *ib.*, **115**, 253, 265, 1917; D. P. Liebenberg and S. Leith, *Journ. S. African Chem. Inst.*, **14**, 47, 1931; for nitric acid and potassium chlorate, see D. P. Liebenberg and S. Leith, *l.c.*; for sodium chlorate, see F. G. Hanley, *Eng. Min. Journ.*, **105**, 385, 1918; for bromine in carbon tetrachloride, see W. S. Allen and H. B. Bishop, *Eighth Internat. Cong. App. Chem.*, **1**, i, 33, 1912; for sodium hydroxide and bromine, see T. M. Drown, *Chem. News*, **43**, 89, 1881.

[7] G. Lunge, *Zeit. anal. Chem.*, **19**, 419, 1880; **20**, 417, 1881; *Zeit. angew. Chem.*, **2**, 473, 1889; *Journ. Soc. Chem. Ind.*, **8**, 966, 1889; *Fifth Int. Congress App. Chem.*, 399, 1906; E. Hintz and H. Weber, *Zeit. anal. Chem.*, **45**, 31, 1906; A. Noaillon, *Zeit. angew. Chem.*, **10**, 351, 1897; H. C. Moore, *Journ. Ind. Eng. Chem.*, **7**, 634, 1915.

[8] G. Chandron and G. Juge-Boirard (*Compt. rend.*, **174**, 683, 1922) say that some sulphur always separates if the temperature exceeds 60°, while at room temperature there is no separation but the time needed for oxidation is much longer.

[9] The residue may be dried, ignited and weighed as a mixture of silica, silicates and sulphates of lead, barium and calcium. With calcareous or magnesian clays, there is a danger of loss as indicated on page 709.

[10] C. Zay (*Stat. sperim. agrar. Ital.*, **49**, 530, 1916; *Chem. Zentr.*, (1), 446, 1917; Kastner, *Ann. Chim. anal.*, (2), **9**, 134, 1927) advises a double precipitation of the iron. E. J. Virgin (*Teknisk Tids. (Kemi)*, **53**, 1, 1923) either dissolves the precipitated ferric hydroxide in hydrochloric acid and precipitates any sulphate in this solution with barium chloride, or reduces the iron with hydroxylamine hydrochloride but does not subsequently remove it.

should occupy about 250 or 300 c.c.[1] Acidify the solution with hydrochloric acid, avoiding an excess. Heat the solution to boiling; remove the flame; add, all at once,[2] barium chloride solution with constant stirring.[3] The addition of too great an excess of barium chloride leads to high results. Let the whole stand about 40 minutes. Decant the clear liquid, filter, wash, ignite and weigh as barium sulphate.[4]

Sulphides Decomposed by Acids.—When the sulphides—say sulphides of the alkalies or alkaline earths—can be decomposed by boiling acids,[5] grind, say, 5 grms. of the powder with water to a thin slurry. Transfer the slurry to a (250 c.c.) gas developing flask (fig. 148) fitted with a stoppered funnel and an exit tube so that any gas generated may be passed through, say, 10 c.c. of a solution of cadmium acetate (or ammoniacal cadmium chloride).[6] Add hydrochloric acid to the mixture in the flask, *via* the stoppered funnel. Warm the contents of the flask and drive off the hydrogen sulphide by a current of air, or preferably hydrogen, which enters through the stoppered funnel. Filter off the precipitated cadmium sulphide through a small paper and wash it once or twice with a 10 per cent. solution of ammonia. Place the filter-paper and precipitate in a conical flask, add about 50 c.c. of water and shake. Now add 5 c.c. of hydrochloric acid (sp. gr. 1·16) and run in a measured excess, say 10 c.c., of a standard solution of iodine. Thoroughly shake for about half a minute
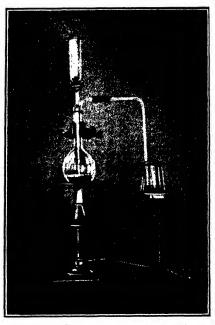
Fig. 148.—Determination of Sulphides.

and titrate the excess of iodine with a standard solution of sodium thiosulphate as indicated on page 376.

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[1] If the volume is greater, concentrate by evaporation.

[2] Compare page 694.

[3] The adsorption error (page 691) is supposed to compensate the loss caused by the solubility of the barium sulphate in the mother liquid—G. Lunge, *Journ. Amer. Chem. Soc.*, **17**, 772, 1895.

[4] The method has often been condemned and often vindicated—P. Jannasch and T. W. Richards, *Journ. prakt. Chem.*, (2), **39**, 333, 1889; (2), **40**, 236, 1889; G. Lunge (with Barbezat and Obregia), *ib.*, (2), **40**, 239, 1889; *Zeit. angew. Chem.*, **2**, 473, 1889; T. S. Gladding, *Journ. Amer. Chem. Soc.*, **16**, 398, 1894; **17**, 397, 1895; **18**, 446, 1896; G. Lunge, *ib.*, **17**, 181, 772, 1895; **18**, 685, 1896; *Zeit. angew. Chem.*, **8**, 69, 1895; **9**, 453, 1896; *Zeit. anorg. Chem.*, **19**, 454, 1899; F. W. Küster and A. Thiel, *ib.*, **19**, 98, 1899; **21**, 73, 1899; G. Lunge and E. Misslin, *ib.*, **21**, 198, 1899; G. Lunge, *ib.*, **21**, 200, 1899; C. Meineke, *Zeit. anal. Chem.*, **38**, 209, 357, 1899; J. Clark, *Journ. Soc. Chem. Ind.*, **4**, 329, 1885; J. Pattinson, *ib.*, **9**, 21, 1890.

[5] F. A. Kuhnlenz, *Chem. Ztg.*, **31**, 835, 1907; F. L. Crobaugh, *Journ. Anal. App. Chem.*, **7**, 280, 1893; T. J. Morrell, *Chem. News*, **28**, 229, 1873.

[6] CADMIUM ACETATE SOLUTION.—Dissolve 25 grms. of cadmium acetate in 200 c.c. of glacial acetic acid, and make the solution up to a litre—F. L. Crobaugh, *l.c.*; O. Herting, *Chem. Ztg.*, **21**, 87, 1897. F. Weil (*Compt. rend.*, **102**, 1487, 1886) used a standard ammoniacal solution of a copper salt. After passing hydrogen sulphide through this solution, it was

There is a danger of losing sulphide when ferric salts are present. The hydrogen sulphide reduces the ferric salts and is itself oxidised. Hinrichsen [1] recommends adding, say, 10 c.c. of a 20 per cent. solution of stannous chloride to the mixture in the generating flask, in order to avoid the error.

Oxidisable Matter in Limestones.—The disintegration of limestones is supposed by some to be related to the amount of oxidisable matter, chiefly pyrites, which they contain,[2] and this is determined by the following process:—Add 25 c.c. of 0·1 N-potassium permanganate to 1 grm. of the dried (110°) and powdered clay in a 250 c.c. Erlenmeyer's flask. When the powder is all moistened, add 100 c.c. of a 10 per cent. solution of sulphuric acid,[3] and shake the flask. If the colour of the potassium permanganate be discharged, add a second 25 c.c. of the permanganate solution. Heat the mixture on a water bath, with occasional shaking, for about half an hour.[4] Run 30 c.c. of 0·1N-oxalic acid into the flask.[5] Let the mixture stay on the water bath a few minutes longer. All the brown manganic compounds should have passed into solution. The excess of oxalic acid is titrated with 0·1N-potassium permanganate. Three one-gram samples should be used. The results are calculated to "oxygen consumed by the limestone." The limestones examined by Peters consumed between 0·048 and 2·120 per cent. of oxygen.[6] 1 c.c. of 0·1N-potassium permanganate gives 0·0008 grm. of oxygen.

§ 339. The Volumetric Determination of Sulphates— Raschig's Process.

Benzidine hydrochloride — $C_{12}H_8(NH_2)_2.2HCl$ — in aqueous solution is hydrolysed in such a way that the solution behaves as if it contained benzidine — $C_{12}H_8(NH_2)_2$ — and hydrochloric acid. If such a solution be titrated with sodium hydroxide, the phenolphthalein will develop a pink coloration after all the acid is neutralised by the soda. The reaction is quantitative. Suppose, further, an excess of benzidine hydrochloride be added to a solution containing, say, sodium sulphate, sparingly soluble benzidine sulphate — $C_{12}H_8(NH_2)_2.H_2SO_4$ — will be precipitated:

$$C_{12}H_8(NH_2)_2.2HCl + Na_2SO_4 = 2NaCl + C_{12}H_8(NH_2)_2.H_2SO_4$$

The excess of benzidine hydrochloride can then be determined by titration with standard alkali. The difference between the titre of the benzidine hydrochloride added to the sulphate solution and that of the benzidine hydrochloride remaining after the precipitation of the benzidine sulphate, represents the "sulphate" in the given solution. This method, due to Müller,

made up to a given volume and an aliquot portion titrated as indicated on page 367 for unprecipitated copper. The difference between the result and the amount of copper originally present represented the amount precipitated by the hydrogen sulphide. R. K. Meade (*Journ. Amer. Chem. Soc.*, 19, 581, 1897) used a solution of a lead salt; G. G. Boucher (*Chem. News*, 75, 121, 1897) used a solution of ferric chloride and titrated the ferrous salt formed by reduction.

[1] F. W. Hinrichsen, *Mitt. k. Material-prüf. Amt.*, 25, 321, 1895.

[2] A. M. Peters, *Journ. Amer. Chem. Soc.*, 25, 143, 1903.

[3] 110 c.c. of sulphuric acid (sp. gr. 1·84) and 1800 c.c. of water.

[4] Experiments show this to be sufficient to oxidise the pyrites, etc.

[5] More if necessary. The volume of oxalic acid is adjusted so that at least 10 c.c. is present in excess of that which has been oxidised by the permanganate. If 25 c.c. of permanganate were added, 30 c.c. of oxalic acid will suffice, provided not less than 5 c.c. of permanganate was reduced; otherwise more oxalic acid will be needed.

[6] Phosphoric acid can be determined, if desired, in the solution by A. L. Emery's volumetric process (*Journ. Amer. Chem. Soc.*, 24, 895, 1902); the insoluble residue is reported as "clay and sand."

presupposes that the sulphate solution is exactly neutral. Since aluminium, iron, zinc and other sulphates do not give neutral solutions, these bases should be absent. Some of the benzidine hydrochloride is also adsorbed by the precipitated sulphate, which leads to high results. The latter difficulty is less marked if the precipitation be made in hot solutions.

Instead of proceeding by Müller's process, it is better to follow Raschig's variation,[1] and titrate the precipitated benzidine sulphate with standard alkali, using phenolphthalein as indicator. The end of the reaction is represented by the equation:

$$C_{12}H_8(NH_2)_2.H_2SO_4 + 2NaOH = Na_2SO_4 + 2H_2O + C_{12}H_8(NH_2)_2$$

The Precipitation.—Pipette, say, 100 c.c. of the neutral or feebly acid solution of the given sulphate, with constant stirring, into 500 c.c. of a cold solution of benzidine hydrochloride [2] in a 600 c.c. Erlenmeyer's flask. Stir the mixture well with a glass rod. The voluminous crystalline precipitate of benzidine sulphate is allowed to settle for about 15 minutes and then separated by suction through a Witt's filter plate (page 91) [3]—4 cm. diameter on the upper side, and 3·5 cm. on the lower side. The supernatant clear liquid is poured through the funnel and the precipitate transferred by shaking the last fifth of the liquid before it is poured into the funnel. Any precipitate which sticks to the sides of the flask in which the precipitation was made can be washed off with some of the clear filtrate, or a wash-bottle filled with benzidine solution can be used. No cracks should appear in the precipitate as the last drop of mother liquid drains from the filter plate. The precipitate is washed twice with 5–10 c.c. of water [4] from a wash-bottle, directed so as to rinse down the sulphate adhering to the sides of the funnel. As the last of the wash-water

[1] F. Raschig, *Zeit. angew. Chem.*, **16**, 617, 818, 1903: **18**, 331, 1905; **19**, 331, 1906; **40**, 864, 1927; C. Friedheim and O. Nydegger, *ib.*, **20**, 9, 1907; L. W. Haase, *ib.*, **40**, 595, 1927; W. Müller, *ib.*, **16**, 653, 1017, 1903; *Ber.*, **35**, 1587, 1902; W. Müller and K. Dürkes, *Zeit. anal. Chem.*, **42**, 477, 1903; J. A. Atanasiu and A. I. Velculescu, *ib.*, **90**, 337, 1932; G. von Knorre, *ib.*, **49**, 461, 1910; *Chem. Ind.*, **28**, 2, 1905; O. Nydegger, *Ueber die Bestimmung der Schwefelsäure durch Benzidin*, Bern, 1907; *Chem. Ztg.*, **52**, 318, 1928; L. W. Haase, *ib.*, **51**, 637, 1927; Vlastimil and M. Matula, *ib.*, **50**, 486, 1926; O. Huber, *ib.*, **29**, 1227, 1905; A. Heczko, *Zeit. anal. Chem.*, **50**, 748, 1911; **51**, 1, 1912; K. K. Järvinen, *Ann. Acad. Scient. Fennicæ*, **2**, A, 4, 1910; 16, 1911; *Chem. Zentr.*, (1), 526, 1912; W. Vaubel, *Zeit. öffent. Chem.*, **20**, 426, 1914; **21**, 1, 1914; F. W. Bruckmiller, *Journ. Ind. Eng. Chem.*, **7**, 600, 1915; E. L. Skau and I. L. Newall, *ib.*, *Anal. Ed.*, **5**, 180, 1933; M. Talenti, *Giorn. Chim. Ind. Appl.*, 8, 611, 1926; G. Testoni, *Annali Chim. Appl.*, **18**, 408, 1928; R. Gauvin and V. Skarzynski, *Bull. Soc. chim.*, (4), **13**, 1121, 1913; G. W. Raiziss and H. Dubin, *Journ. Biol. Chem.*, **18**, 297, 1914; C. H. Fiske, *ib.*, **47**, 59, 1921; O. Rosenheim and J. C. Drummond, *Biochem. Journ.*, **8**, 143, 1914; J. C. Drummond, *ib.*, **9**, 492, 1915; P. L. Hibbard, *Soil Sci.*, **8**, 61, 1919; F. W. Heyl and B. Fullerton, *Journ. Amer. Pharm. Assoc.*, **12**, 617, 1933; M. Chatron, *Journ. Pharm. Chim.*, (8), **13**, 244, 1931; E. Lobstein and M. Angel, *Ann. Chim. anal. Chim. appl.*, (2), **15**, 389, 1933. *Cf.* A. Mutschin and R. Pollak, *Zeit. anal. Chem.*, **106**, 385, 1936; **107**, 18, 1936; **108**, 8, 309, 1937.

[2] BENZIDINE HYDROCHLORIDE.—Rub 40 grms. of benzidine thoroughly with 40 c.c. of water and wash the "slip" into a litre flask with about 750 c.c. of water. Add 50 c.c. of concentrated hydrochloric acid (sp. gr. 1·19) and, when all is dissolved to a clear brown solution, fill the flask up to the litre mark with water. If the solution be turbid, filter. For use, this solution is diluted with twenty times its volume of water. 150 c.c. will suffice for the precipitation of 0·1 grm. of H_2SO_4. Brown flecks may separate from the solution on long standing. These do no particular harm.

[3] The filter plate is covered with two discs of moistened filter-paper. The discs of filter-paper are 4·6 cm. in diameter. The projecting 3 mm. rim of the filter-paper discs is carefully pressed against the sides of the funnel by means of a glass rod with a square end. Successful work depends upon the tight closing of the joint between the funnel and the filter-paper.

[4] The benzidine sulphate is slightly soluble in water. By proceeding in this manner, the loss from this cause can be reduced to a minimum.

drains off, the filtration flask is disconnected from the pump.[1] This must be done before the precipitate contracts to a more or less dry silver-grey skin.[2]

The Transfer of the Precipitate to the Titration Flask.—The funnel is then inclined at an angle of about 45° and the filter plate and precipitate are turned over on the side of the funnel, with the plate uppermost, by pushing a glass rod through the stem of the funnel. The filter plate is removed and the precipitate transferred to a 250 c.c. Erlenmeyer's flask by the aid of the glass rod. The filter-paper is squeezed into a roll and also dropped into the flask. Any benzidine sulphate adhering to the funnel is washed into the flask with a vigorous jet of water. In all, about 25 c.c. of water should be used for the transfer. If any particles of the precipitate remain on the funnel, it is best to wipe them off with a small swab of filter-paper and transfer the latter to the flask. The benzidine sulphate should now be all in the flask. Close the flask with a rubber stopper and shake it thoroughly, so as to form a kind of slurry—precipitate, filter-paper and water—quite free from lumps of benzidine sulphate. Remove the stopper from the flask and wash back any adhering particles of the sulphate with a few drops of water.

The Titration.—Add about 2 c.c. of phenolphthalein [3] and titrate the solution with 0·1N-sodium hydroxide until the red colour of the indicator appears. Warm the flask until the colour has disappeared and continue the titration until a faint red appears. Again heat the flask until the liquid boils, so as to expel any carbon dioxide. The end of the titration is shown by the persistence of a faint red colour in the liquid.[4] At the end of the titration one or two drops of 0·1N-hydrochloric acid should remove the colour and this should not reappear after boiling two minutes.

EXAMPLE.—100 c.c. of a solution of sulphate were poured into 500 c.c. of the benzidine solution. The benzidine sulphate slurry needed 49·15 c.c. of 0·1N-NaOH to develop the proper coloration. Here, 49·15 c.c. of 0·1N-NaOH represent 0·2410 grm. of H_2SO_4. As a matter of fact, the solution really contained 0·2430 grm. of H_2SO_4. Hence, the error, 0·0020 grm., approached 0·9 per cent. But closer results can be obtained after a little practice in the method.

Modification in the Presence of Iron Salts.—Nydegger tried the effect of slightly acidifying the solution with hydrochloric, nitric and acetic acids; the effect of additions of potassium, ammonium, copper, aluminium, zinc and chromium chlorides, potassium nitrate, sodium acetate, ammonium, zinc, manganese, cobalt, copper, aluminium and ferrous sulphates. The results were quite satisfactory. It is generally considered that no more iron should

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[1] Make sure that all the sulphuric acid has been precipitated, by testing the filtrate with barium chloride solution. No precipitate should be produced, but after standing 15 minutes a slight turbidity will probably appear owing to the decomposition of the trace of benzidine sulphate in the filtrate. The loss from this source is very small, and it is compensated by the slight excess of the 0·1N-NaOH—one or two drops, corresponding with 0·12 to 0·2 per cent. of sulphur—required for colouring the phenolphthalein adsorbed by the pulp of the filter-paper in the flask during the titration.

[2] Dried benzidine sulphate cannot be properly dispersed through the water and, in consequence, it will be but slowly decomposed by the sodium hydroxide during the titration. The results will then be low. If by accident undecomposed flakes of benzidine sulphate should appear in the liquid, boiling with a small known excess of sodium hydroxide will effect decomposition. The excess of soda can be determined by back titration with standard acid.

[3] This unusually large amount of indicator is needed because some of the indicator is adsorbed by the paper pulp in the flask.

[4] The tint can be recognised through the fibres of the filter-paper, but, if necessary, the paper can be allowed to settle to facilitate the observation of the end coloration. An intense red colour shows over-titration.

be present than is represented by Fe : S. If ferric iron be present, some will be occluded with the precipitated benzidine sulphate and spoil the result.[1] The ferric iron should be reduced to the ferrous condition before adding the benzidine hydrochloride. The reduction is best made with hydroxylamine hydrochloride, as described below. Satisfactory results can then be obtained with both copper and iron pyrites.

For pyrites, Raschig recommends the following process:—0·8 grm. of finely powdered pyrites is placed in a dry 200 c.c. Erlenmeyer's flask with 5 c.c. of fuming nitric acid. Heat the mixture on a water bath, with a funnel in the neck of the flask to prevent loss by spurting. The pyrites should be decomposed in about half an hour. Add 30 c.c. of water and warm the mixture a short time to dissolve the iron salts. Dilute the solution—with or without the removal of the solid residue—to the 100 c.c. mark in a measuring flask. Pipette 20 c.c. of this solution into a 600 c.c. beaker, add 10 c.c. of a 1 per cent. solution of hydroxylamine hydrochloride and 500 c.c. of the benzidine solution. Stir the mixture with a glass rod and let it stand 15 minutes. Then proceed as described above.[2]

Errors.—With a little practice, the results obtained by this method for sulphur in substances such as pyrites, rival in accuracy results with the barium chloride process. The more important sources of error are: (1) the slight solubility of the benzidine sulphate in water; (2) slight adsorption of benzidine hydrochloride by the precipitated benzidine sulphate; (3) imperfect titration due to the "balling" of the sulphate when it is overdried; (4) imperfect precipitation of sulphate through using insufficient benzidine hydrochloride; and (5) the need for a slight excess of the 0·1N-NaOH solution, owing to adsorption of the indicator by the paper pulp. Some of these errors compensate one another. The time needed for the determination of sulphur in pyrites by this method is something less than one and a half hours, but the method is time-saving only when a number of determinations under similar conditions has to be made.

§ 340. Hinman's Barium Chromate Process.

In this method[3] a measured excess of a standard solution of barium chromate[4] is slowly run into the boiling, faintly acidic solution of the sulphate, which should not contain more than 2 per cent. of sulphur trioxide. The solution is boiled for a few minutes and then made alkaline by the addition of ammonium hydroxide, whereby the excess of barium chromate is precipitated. The mixed precipitate of barium sulphate and chromate is filtered off and well washed with hot water. The soluble chromate in the filtrate and washings, produced by the reaction—

$$Na_2SO_4 + BaCrO_4 = Na_2CrO_4 + BaSO_4$$

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[1] See L. W. Haase (*Zeit. angew. Chem.*, 40, 595, 1927) for the effect of ferric, magnesium and calcium salts on the accuracy of the method.

[2] The number of c.c. of 0·1N-NaOH used represents the per cent. of sulphur in the pyrites. The other four-fifths of the solution in the measuring flask can be used for check determinations.

[3] C. W. Hinman, *Amer. Journ. Sci.*, (3), 14, 478, 1877; L. W. Andrews, *Amer. Chem. Journ.*, 11, 567, 1889; J. D. Pennock and D. A. Morton, *Journ. Amer. Chem. Soc.*, 25, 1265, 1903; G. Bruhns, *Zeit. anal. Chem.*, 45, 573, 1906; M. Holliger, *ib.*, 49, 84, 1910; D. Köszegi, *ib.*, 77, 203, 1929; R. Schmidt, *ib.*, 82, 353, 1930; H. North, *Amer. Journ. Pharm.*, 86, 249, 1914; G. Nachtigall and F. Raeder, *Arch. Hyg.*, 100, 31, 1928; J. R. Andrews, *Ind. Eng. Chem. Anal. Ed.*, 3, 361, 1931.

[4] 4 grms. of the pure, precipitated salt are dissolved in 1000 c.c. of 1·0N-hydrochloric acid.

is determined by acidifying the solution with sulphuric acid, adding an excess of potassium iodide and titrating the liberated iodine with 0·1N-sodium thiosulphate. 1 c.c. of 0·1N-sodium thiosulphate represents 0·002669 grm. SO_3. Alternatively, the soluble chromate can be determined by the ferrous sulphate-permanganate process, as given on page 530.

§ 341. The Determination of the Soluble Salts in Clays.

The "soluble salts" in clays are responsible for certain manufacturing difficulties, and consequently it may be of great importance to determine their amount and nature. In such cases the clay is boiled with water and the insoluble residue removed by filtration through filter-paper, or by settling.[1]
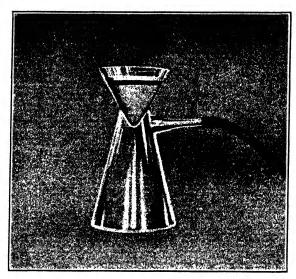
FIG. 149.—Filtration through Porous Cone.

It is, however, at this stage that the practical difficulties arise, as the clay is sometimes so finely divided that the solid cannot be separated from the liquid by filtration even through a dozen filter-papers, and some clays take so long to settle that the solid matter appears to be in permanent suspension. The turbid filtrate may be evaporated to dryness on a water bath and dried at 110°. The residue may then be extracted with water, and the filtrate will usually be quite clear.[2]

The most satisfactory method is to filter the solution through biscuit pottery or alundum ware,[3] glass Gooch crucibles with fine grade, sintered

[1] R. Fresenius, *Anleitung zur quantitativen chemischen Analyse*, Braunschweig, **2**, 666, 1887; London, **2**, 521, 1900.

[2] J. Post, *Chemisch-technische Analyse*, Braunschweig, **2**, 98, 1906.

[3] L. J. Briggs (*Bull. U.S. Agric. Dept.*, **19**, 31, 1902) and O. Schreiner and G. H. Failyer (*ib.*, **31**, 12, 1906) passed the solution through a Pasteur-Chamberlain water filter by means of a force-pump. J. W. Mellor, *Trans. Cer. Soc.*, **5**, 54, 1906; *Pot. Gaz.*, **32**, 1049, 1907; C. E. Munroe, *Amer. J. Science*, (3), **1**, 336, 1871; *Chem. News*, **24**, 79, 1871; F. Klein, *Amer. J. Pharm.*, **83**, 342, 1911; E. B. Forbes, *Journ. Ind. Eng. Chem.*, **4**, 544, 1912; G. L. Spencer, *ib.*, **4**, 614, 1912; M. A. Williamson and P. A. Boeck, *ib.*, **4**, 672, 1912; H. O. Anderson, *ib.*, **3**, 42, 1911; P. E. Brown and E. H. Kellogg, *ib.*, **7**, 686, 1915; W. B. Hicks, *ib.*, **6**, 829, 1914; L. E. Saunders, *Met. Chem. Eng.*, **9**, 257, 1911; W. Pukall, *Ber.*, **26**, 1159, 1893; *Chem. News*, **72**, 86, 1895.

glass filter discs fused into the base, paper pulp, or similar filtration media.[1]
A Gooch crucible in which the bottom of the crucible has neither been per-
forated nor glazed can be used, or a biscuit crucible can be glazed inside and
outside to within half a centimetre from the bottom. This crucible is fitted
up like the regular Gooch crucible. Instead of using crucibles with a biscuit
bottom, cones of porous earthenware can be used. These can either be fitted
inside a suitable funnel, or fitted to the funnel-like neck of a Walther's
filtration flask,[2] as indicated in fig. 149. The porous cone is fitted into the
funnel by means of a rubber ring, so as to make a tight joint. There is then
no need for the perforated stopper.[3] Fig. 149 makes the arrangement clear.

Rümpler's filtration cups,[4] made of thick, porous
filter-paper, are sometimes convenient for filter-
ing solutions which give trouble with ordinary
filter-paper. Care should be taken to get the
crucible [5] and filter-paper to fit as indicated in
the diagram, fig. 150. The inner layer in the
diagram represents a section of the Rümpler's
cup, and the outer layer, the crucible.

To conduct an experiment: boil gently about
5 grms. of the finely powdered clay with about
250 c.c. of distilled water in a resistance glass
flask for about half an hour. Cover the mouth
of the flask with a watch-glass to minimise loss
by evaporation and, if necessary, add more water
from time to time. After the clay has settled
somewhat, pour the liquid through the biscuit
earthenware cone, fig. 149. The pump is now
turned on and the cone is kept filled with liquid.

FIG. 150.—Filtration by
Rümpler's Shells.

The clay is washed with hot distilled water, and the
filtrate is evaporated to dryness in a weighed dish. The residue is dried at,
say, 110°, and its amount is expressed as a percentage. The clay sometimes
clogs the pores of the cone, so that the process of filtration is extremely slow.
In that case, the liquid can be filtered through a Rümpler's cup [6] (fig. 150),
and afterwards through the biscuit cone. The washing should be conducted
until a few drops of the liquid running from the clay leave no perceptible
residue when evaporated to dryness on platinum foil. The result of this
experiment does not necessarily represent the whole of the soluble salts in the
clay. Some may be adsorbed by the clay in such a way that they can only
be removed, if at all, by an extremely prolonged washing.[7] However, the
adsorbed salts which are not removed by washing are not of importance from
the point of view of "soluble salts," and the result actually obtained is the
datum required. The silica, alumina, etc., can be determined in the residue
in the ordinary way (pages 147 et seq.).

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[1] E Greiner, *Sprech.*, **42**, 399, 1909.

[2] J. Walther, *Pharm. Centr.*, 530, 1898.

[3] The air in the rubber rings, under low pressure inside the flask—powerful suction—is
apt to expand and burst the ring. Solid rubber rings do not work so well unless they are
made of soft, very yielding rubber.

[4] A. Rümpler, *Deut. Zuckerind.*, **29**, 21, 1904.

[5] The cups fit crucibles 6·5 cm. high, 5·4 cm. upper diameter and 3·2 cm. diameter at the
base (outside measurements).

[6] Or through a fine grade filter-paper, then filtering the more or less turbid liquid through
a filter crucible.

[7] For the removal of salts from solution by adsorption during filtration through earthen-
ware filters, see W. B. Hicks, *Ind. Eng. Chem.*, **6**, 829, 1914.

§ 342. The Determination of Sulphates by the Turbidity Process.

The sulphates in the clear solution, say, from the preceding operation, can be determined as barium sulphate by the method of page 703; or, more rapidly, if a number of determinations has to be made, by comparing the turbidity of a solution containing a known amount of barium sulphate in suspension with that produced in the given solution by the addition of barium chloride. The solutions must be dilute enough to produce an opalescent and not a settling precipitate. The opalescence depends largely on the size of the particles precipitated in the solution and this, in turn, is determined by the physical condition of the solution—*e.g.* the temperature and nature of other salts in solution. The method gives fairly satisfactory results for industrial work when speed is a vital factor. The standard and the solution under investigation should not be widely different in strength and, in consequence, a preliminary comparison should be made in test tubes. If the solution under investigation gives a very much more turbid solution than the standard, it should be diluted; and conversely. The solutions must not be diluted *after* the addition of barium chloride.[1]

Standard Solution.—A stock solution of calcium sulphate is made by dissolving 0·8962 grm. of calcium sulphate—$CaSO_4.2H_2O$—in a litre flask, so that 1 c.c. contains the equivalent of 0·0005 grm. SO_4. Make 25 c.c. of this stock solution up to a litre to give a standard solution. Pipette, say, 100 c.c. of the standard solution into a tightly stoppered wide-mouthed bottle. Add 0·1 to 0·2 grm. of powdered, crystalline barium chloride and shake. Pipette 50 c.c. of this solution into a Nessler's glass surrounded by black paper or a black velvet jacket.

Test Solution.—Acidify the filtrate from, say, 10 grms. of clay with hydrochloric acid and make up to 250 c.c. with water. Pipette, say, 100 c.c. of this solution into a wide-mouthed bottle and treat as just described for the standard solution.

Comparison.—Place the test solution in a burette and run it into a Nessler's glass fitted with a black jacket, as indicated above, until the solutions in the two Nessler's glasses appear to have the same turbidity. The comparison is made with the Nessler's glasses resting upon a plate of clear glass supported over a sheet of black paper.

Calculations.—Suppose that the two solutions have the same turbidity when 13 c.c. have been run from the burette. Then 13 c.c. of the test solution have the same turbidity as 50 c.c. of the standard, *i.e.* as 0·000625 grm. SO_4. Hence, 250 c.c. will have the equivalent of :—

$$250 \times 0.000625/13 = 0.012 \text{ grm. } SO_4$$

Thus, 10 grms. of the clay have the equivalent of 0·012 grm. of SO_4; or, 0·12 per cent. SO_4; or 0·17 per cent. $CaSO_4$.

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[1] T. W. Richards and R. C. Wells, *Amer. Chem. Journ.*, **31**, 235, 1904; *Journ. Amer. Chem. Soc.*, **27**, 459, 1905; J. I. D. Hinds, *ib.*, **18**, 661, 1896; **22**, 269, 1900; *Chem. News*, **73**, 285, 299, 1896; D. D. Jackson, *Journ. Amer. Chem. Soc.*, **23**, 799, 1901; S. W. Parr and C. H. McClure, *ib.*, **26**, 1139, 1904; P. A. Kober, *ib.*, **35**, 290, 1585, 1913; S. W. Parr, W. F. Wheeler and R. Berolzheimer, *Journ. Ind. Eng. Chem.*, **1**, 689, 1909; S. W. Parr and W. D. Staley, *ib.*, *Anal. Ed.*, **3**, 66, 1931; R. T. Sheen, H. L. Kahler and E. M. Ross, *ib.*, **7**, 262, 1935; R. Seifert, *Süddeutsche Apoth. Ztg.*, **72**, 523, 1932; F. Dienert, *Compt. rend.*, **158**, 1117, 1914; J. T. Marshall and H. W. Banks, *Proc. Amer. Phil. Soc.*, **54**, 1, 1915; H. H. Willard and R. Schneidewind, *Trans. Amer. Electrochem. Soc.*, **56**, 333, 1930; L. E. Stout and A. W. Petchaft, *ib.*, **56**, 351, 1930; D. R. Williams, *Rock Products*, **30**, No. 8, 54, 1936; R. B. Rudy, *Journ. Research Nat. Bur. Standards*, **16**, 555, 1936.

The most important disturbing influences arise from the introduction of side-lights during the comparison of the turbidities; and the mode of precipitation —-hot or cold, with the solid salt or with an aqueous solution—-and whether the readings be made at once or after the solution has stood some time. Consequently, *it is necessary to follow rigorously the same procedure in preparing the standard and the test solutions.*

Instead of using Nessler's glasses for the comparison, Richards and Wells use a nephelometer for comparing the turbidities of different solutions. Hinds and Jackson read the depth of the turbid liquid at which a standard sperm or wax candle flame just ceases to be visible; the corresponding amount of SO_4 is read directly from a standard table prepared by empirical observations with solutions of known strength.[1] The cylinders are 3·5 cm. wide, 20 cm. high, and graduated from below upwards. The cylinder is supported over the lighted candle and the liquid, with the precipitate in suspension, is run in until the tip of the candle flame just disappears. In the Burgess-Parr turbidimeter, fig. 151, a hollow tube, fitted with an eye-piece and an optical glass base, can be moved upwards or downwards by means of a ratchet in a cylinder which contains the test solution. This cylinder is also provided with an optical glass bottom and it is fixed over a small electric lamp, maintained at a constant voltage. The tube is racked into such a position that the red filament of the lamp just becomes invisible. The distance between the two optical glass bases is then read on a millimetre scale. In other types of instruments the depth of liquid is kept constant and the voltage of the lamp varied until the glowing filament disappears.
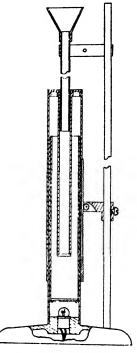
FIG. 151.—Burgess-Parr Turbidimeter.

§ 343. The Amount of Barium Salt required to make the Soluble Sulphates in a Clay Innocuous.

Boil 22·4 grms. of the clay [2] in a long-necked flask with a litre of water. The soluble sulphates pass into solution. Add 1 c.c. of a standard solution of barium chloride containing 10 grms. $BaCl_2$ per litre. Shake the contents of the flask and pipette 2 c.c. into a small funnel, fitted with a close-packed filter-paper, over a test tube. This test tube is labelled No. I. Add another cubic centimetre of the barium chloride solution to the contents of the flask, shake and transfer 2 c.c. to a second test tube, labelled No. II. This operation is repeated with a series of test tubes ranged in order so that each tube represents 1 c.c. more barium chloride solution than the tube immediately preceding, and 1 c.c. less than the tube immediately succeeding. Add about 3 drops of dilute sulphuric acid to each test tube. That tube in which a turbidity first

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[1] J. I. D. Hinds gives for SO_3 the relation $y = 0.0482 \div x$, where x is the cylinder reading, and y the percentage value of SO_3 sought; and for CaO when the lime is precipitated as calcium oxalate $y = 0.036 \div (x - 0.3)$. Different cylinders, and different amounts of raw material, would naturally require different formulæ.

[2] Air-dried, or natural undried clay, or clay dried at 110°.

appears shows the tube which contains more than sufficient barium chloride to react with the sulphates. For instance, suppose that this is tube No. VI., with 6 c.c. of barium chloride; and that the preceding one, No. V., with 5 c.c., is clear. The end of the titration is somewhere between these two tubes, say 5·5 c.c.[1]

Practice[2] shows that with the above proportions every cubic centimetre represents 1 lb. of *anhydrous* barium chloride to be mixed with a ton of clay to transform the soluble sulphates into insoluble and inert barium sulphate. Hence, in the example under consideration, 5½ lbs. of barium chloride are needed per ton of clay. If barium carbonate is used instead of the chloride to precipitate the soluble sulphates, an amount of it should be taken equal to twice the calculated quantity of chloride[3]; thus in the above case 11 lbs. will be needed.[4]

The results agree fairly well with practice, although the method has many faults. If much more than 20 c.c. of barium chloride be needed, the soluble salt difficulty cannot be cured by the barytes method.

Seger and Cramer[5] used a more elaborate apparatus than that just indicated, but it requires less expert manipulation. The results are similar. Some clays—*e.g.* Wetley marl—give liquids very difficult to filter clear and it is not then easy to determine the end of the barium chloride titration by the turbidity of the filtered solution. In that case, it is necessary to separate the solution from the clay by filtration through biscuit ware, as indicated on page 716.

Distinction between Native and Precipitated Barium Carbonate.—Native ground barium carbonate, witherite, is far less effective in removing the soluble sulphates than is the precipitated product and the latter should always be used. There is no single test whereby witherite can be conclusively distinguished from the precipitated carbonate, but by a combination of tests it is usually possible to discriminate between them. Some specimens of witherite are greyer in colour than the synthetic product and on solution in dilute hydrochloric acid leave a larger, denser and darker residue, though much depends on the source of the mineral and its subsequent history. Under a microscope, precipitated barium carbonate shows crystals of almost uniform size, whereas the crystal fragments from witherite are usually larger and more irregularly graded. Continued wet grinding may reduce witherite to such a fine state of division that it is indistinguishable from the precipitated material under a microscope, but this contingency is somewhat remote in a commercial sample of the ground mineral. Sodium carbonate is commonly used in the preparation of commercial precipitated barium carbonate and, in the subsequent washing, the whole of the precipitant will rarely, if ever, be removed. Hence, if the filtrate obtained after boiling a few grams of the sample with distilled water gives an alkaline reaction, this is good evidence that the material is of synthetic origin, since witherite on similar treatment gives a neutral filtrate.

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[1] C. Beringer and J. J. Beringer, *Chem. News*, 59, 41, 1889; R. Wildenstein, *Zeit. anal. Chem.*, 1, 432, 1862.

[2] B. Kerl, *Handbuch der gesammten Tonwaarenindustrie*, Braunschweig, 71, 523, 1907.

[3] Relatively more of the insoluble carbonate is needed because of the mixing difficulty. The soluble chloride is relatively easily brought in contact with the sulphates.

[4] B. Kerl (*l.c.*) recommends adding three-quarters of the calculated quantity of barium chloride and barium carbonate equal to twice the deficiency in chloride. For example: calculated, 10 lbs. BaCl$_2$; used, 7·5 lbs. BaCl$_2$ and 5 lbs. BaCO$_3$.

[5] H. A. Seger and E. Cramer, *Tonind. Ztg.*, 18, 637, 1894; *Hilfs-Geräte für Beaufsichtigung und Vervollkommnung des Betriebes von Ziegeleien*, Berlin, 96, 1911.

CHAPTER XLIII.

THE DETERMINATION OF THE HALOGENS.

§ 344. The Detection of Fluorides.

There is no universally applicable direct test for fluorides in silicates.[1] The two most important of the older reactions available for qualitative tests are (1) the evolution of hydrogen fluoride, which occurs when a fluoride is heated with concentrated sulphuric acid. The reaction is expressed in chemical symbols: $CaF_2 + H_2SO_4 = CaSO_4 + 2HF$. The presence of the hydrogen fluoride is recognised by its action on glass—the so-called "etching test." (2) If silica or a silicate be present, most of the hydrogen fluoride reacts with the silica to form silicon tetrafluoride—SiF_4—as indicated by the symbols: $SiO_2 + 4HF = 2H_2O + SiF_4$. The silicon fluoride will not etch glass, but it will react with a drop of water, forming hydrofluosilicic and silicic acids. Thus, in symbols: $3SiF_4 + 3H_2O = 2H_2SiF_6 + H_2SiO_3$. The latter gives the drop of water a turbid appearance—the so-called "hanging drop test." If the silicate contains fluorides which are not attacked by the concentrated acid, it is necessary to get the fluoride in a form—say, as calcium fluoride—susceptible to attack before either test can be applied.

Colorimetric tests are now available (see page 724).

The Separation of Fluorine as Calcium Fluoride from Fluo-silicates not attacked by Sulphuric Acid.[2]—Mix the fluo-silicate with about eight times its weight of sodium carbonate, fuse the mixture in a platinum crucible and, when the mass is cold, extract with water. The solution contains sodium fluoride and sodium silicate. Remove the silica by adding an excess of Schaffgotsch's solution and allow the mixture to stand overnight in a warm place. Filter and evaporate the filtrate to a small volume. Add a little methyl red and carefully add dilute hydrochloric acid from a burette until the yellow colour of the indicator just changes to red. To make sure the mass is just neutralised, and no excess of acid is present, heat the solution to boiling—should a yellow colour reappear, add acid drop by drop until a red tinge is visible. Add an excess of a solution of calcium chloride and again boil the solution. Filter off the precipitate, wash, dry and ignite in a platinum crucible. Add acetic acid and evaporate to dryness. This converts any calcium carbonate into soluble acetate. Rub up the mixture with water and filter off the insoluble

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[1] *Fluoriné in Reagents.*—P. Carles (*Bull. Soc. chim.*, (4), 13, 553, 1913; *Ann. Chim. anal.*, 19, 101, 1914) finds that sulphuric and hydrochloric acids are generally free from fluorine, but nitric acid usually contains it. To remove the fluorine, redistil and reject the first two-thirds of the distillate. Potassium and sodium nitrates usually contain fluorine; they can be freed by boiling with barium nitrate and barium hydroxide and removing the excess of the barium salt by a current of carbon dioxide. Barium hydroxide usually contains insoluble fluorides, the alkali bicarbonates are rarely free from fluorine and ammonium carbonate always contains it.

[2] F. P. Treadwell, *Analytical Chemistry*, New York, 1, 352, 1903.

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calcium fluoride. Dry and burn off the filter-paper. The powder is then ready for the etching test.

The Etching Test.—This is available for fluorides which are free from silica or silicates and which are attacked by concentrated sulphuric acid. A small clear glass plate, free from scratches, is thoroughly cleaned and warmed. A little molten wax [1] is poured on to the warm plate and the excess drained off, so that a thin uniform layer of wax remains spread over the plate. The plate is allowed to cool in a horizontal position. While the wax is still warm, make a small + on the wax with a pointed instrument, so as to lay bare, but not to scratch, the glass.[2]

The powder under investigation is placed in a platinum crucible,[3] along with 2 or 3 c.c. of concentrated sulphuric acid.[4] Warm the upper edge of the crucible cautiously and quickly with a small flame. Press the glass plate, waxed side downwards, upon the crucible so that the cross is in the centre and the crucible is sealed to the plate when the wax cools. The crucible is supported in a hole in a piece of thick asbestos board, cut so as to fit the crucible tightly. Put two or three drops of water on the glass plate and press the end of a metal condenser [5] (fig. 152) down on the plate.[6] The disposition of the apparatus will be obvious from fig. 152, where *C* is the condenser, *B* the glass plate, *A·* the asbestos board and crucible and *D* the micro-burner for heating the crucible.[7] When the mixture has been heated for about half an hour over a small flame—9 mm. high and 6 mm. below the bottom of the crucible — remove the condenser and

Fig. 152.—Etching Test for Fluorides.

plate. Warm the plate a little and wipe off the wax. Clean the plate on both sides with polishing powder which will not scratch the glass. Examine the plate by reflected light for any etching. A test should not be considered positive unless the cross can be seen from both sides of the glass.[8]

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[1] Beeswax or, better, melt together equal weights of carnauba wax and paraffin wax, and thoroughly mix by stirring.

[2] The marks are best made about 1 mm. wide and the two arms of the cross about 4 mm. long. The ends of the arms of the cross should be marked on the uncoated side of the glass with a scratching diamond or file.

[3] It is best to have everything in the crucible quite dry, since the etching is not always so well defined if moisture be present.

[4] The sulphuric acid must be free from fluorides. This can be determined by a blank experiment.   If fluorides be present, they can be removed by diluting the acid with water and evaporating down to its former volume.

[5] A shaving soap or similar container can easily be adapted for this purpose.

[6] The etching is frequently done on the convex side of a waxed watch-glass and a little cold water is placed in the watch-glass to prevent the wax melting.

[7] It is advisable every now and again to put a couple of drops of water on the plate round the edge of the condenser to keep the wax from melting.

[8] Sulphuric acid may corrode the glass so that the cross can be seen when the glass is breathed upon. The scouring with the polishing powder usually removes the sulphuric acid "stain."

Woodman and Talbot[1] state that their process, as described above, will give a recognisable test, that is, the cross will be visible from both sides of the plate, with 1 : 5,000,000 parts of fluorine. The temperature is an important factor. Attempts have been made to estimate the amount of fluorine from the intensity of the etching,[2] and Woodman and Talbot obtained promising results by varying the temperature of the crucible. Thus:

Table LXVII.—Test Analyses for the Detection of Fluorine.

Temperature.	Distinguishes one part of fluorine per
79– 82°	25,000– 100,000
113°	100,000– 1,000,000
136°	1,000,000– 5,000,000
173–178°	5,000,000–25,000,000
213–218°	25,000,000 or more

This test is of very limited application so far as the silicate industries are concerned, because the complete absence of silica is essential if but small quantities of fluorine are in question.[3]

The Hanging Drop Test.—About half a gram of the thoroughly dried powder under investigation is well mixed with about 0·1 grm. of dried precipitated silica and placed in the bottom of a test tube about 5 cm. long and 1 cm. wide. The test tube *A* (fig. 153) is fitted with a one-hole rubber stopper, *B*. The stopper carries a piece of glass tubing, *C*, closed at the upper end and inserted in the stopper so that the open end of the tube extends about 3 mm. below the stopper. The glass tubing *C* is nearly filled with two drops of water, *D*, from a small pipette. The stopper and everything else inside the test tube must be quite dry. Pipette 1 or 2 c.c. of concentrated sulphuric acid into the test tube, and immediately insert the stopper without dislodging the drop of water in the little tube. Place the test tube in a beaker of water. Heat the water to boiling and, after 20–30 minutes' heating, if the substance contains appreciable quantities of fluorine, a heavy gelatinous ring of silicic acid will be found at

Fig. 153.—Hanging Drop Test for Fluorides.
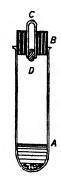
[1] A. G. Woodman and H. P. Talbot, *Journ. Amer. Chem. Soc.*, 28, 1437, 1906; 29, 1362, 1907; C. Blarez, *Chem. News*, 91, 39, 1905; A. E. Leach, *Ann. Rep. Mass. State Board of Health*, 36, 309, 1905; G. W. M. Williams, *Chem. World*, 1, 255, 1912; B. Fetkenheuer, *Wiss. veröffentl. Siemens-Konzern*, 1, (3), 177, 1922; S. K. Hagen, *Mikrochem.*, 15, 313, 1934; W. Partridge, *Analyst*, 44, 234, 1919.

[2] H. Ost, *Ber.*, 26, 152, 1893; but see O. Renner, *Ueber die Bestimmung des Fluors*, Weida, i. Th., 1912; G. Forchhammer, *Edin. Phil. Journ.*, 48, 345, 1850; E. Oliver, *Rev. universelle Mines*, 14, 25, 1922; A. Mayerhofer and A. Wasitzky, *Biochem. Zeit.*, 204, 62, 1929; L. Fresenius, K. Schröder and M. Frommes, *Zeit. anal. Chem.*, 73, 65, 1928; H. Spielhaczek, *ib.*, 100, 184, 1935.

[3] For the spectrographic detection of fluorine, see J. Papish, L. E. Hoag and W. E. Snee, *Ind. Eng. Chem. Anal. Ed.*, 2, 263, 1930. For the detection of fluorine with ferric ferrocyanide, see L. Kul'berg, *Journ. Gen. Chem. (U.S.S.R.)*, 4, 1440, 1934; by lanthanum, J. Fischer, *Zeit. anal. Chem.*, 104, 344, 1936; P. Giammarino, *ib.*, 108, 196, 1937.

the mouth of the little tube carrying the drop of water.[1]   With a little practice, or by conducting the test simultaneously with powders containing known amounts of fluoride, a rough idea can be formed of how much fluorine is present, and whether the compound is worth a quantitative investigation by, say, Oettel and Hempel's process (page 739).   Carbonates should not be present, or the stopper may be blown from the tube or the tube burst.   Hence, carbonates should be destroyed by calcination before the test is applied.

De Boer's Test.—The lakes formed between most metals and alizarin-sulphonic acid are discharged by an excess of hydrochloric acid, except that given by zirconium, which yields a reddish-violet solution.   Fluorides convert this coloured solution into a yellow one by the removal of the zirconium as a complex fluoride and, according to de Boer, the reaction is so sensitive that it will detect one part of fluorine in a million of water.[2]

There are various ways in which the test is applied.   Pavelka [3] uses test papers made by moistening filter-paper with basic zirconium chloride to which an excess of an alcoholic solution of alizarin has been added.   The dry papers are moistened with one drop of 50 per cent. acetic acid and then one drop of the suspected solution is applied.   In the presence of 0·01 mgrm. of fluorine, a yellow stain appears on the red paper.   With insoluble fluorides, the powdered material is shaken with 5 c.c. of aqueous hydrochloric acid, containing 0·5 to 1 grm. of borax, and a drop of the mixture is taken for the test.   Alternatively, the material is heated with silica and sulphuric acid and the test paper is held in the vapours.   Alimarin [4] mixes 0·2 to 0·5 grm. of the finely ground substance with 1 grm. of boric oxide and heats the mixture in a hard glass test tube, as in the Penfield water test (see page 641).   If the substance contains fluorine, the liquid in the bulb will contain hydrofluoboric acid, HBF_4, which is detected by its bleaching action on the zirconium lake either in solution [5] or on test papers.   This method is reported to detect 0·008 mgrm. of fluorine in 0·3 grm. of rock.   Sulphuric, oxalic and phosphoric acids, and borates, interfere and strong oxidising agents must be reduced, or they will destroy the dye.   Kolthoff and Stanby [6] have developed the test so that as little as 0·005 mgrm. of fluorine can be detected in the presence of any metal or acid radical.   A hard glass distillation flask of about 150 c.c. capacity is

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[1] W. Kopp (*Ber. König. Sächs. Ges. Wiss.*, 37, 1882) has modified the test. A small flask with exit tube is thoroughly dried, and a mixture of the finely powdered material with the precipitated silica is placed in the flask.   Pour an excess of concentrated sulphuric acid into the flask.   One end of a delivery tube is fitted to the flask, and the other end dipped into a small cylinder containing a decigram of colourless aniline (or ammonia) in 30 c.c. of water.   Heat the flask to 50° or 60°.   A white deposit about the part of the delivery tube which dips into the aniline indicates the presence of fluorine.   The white glistening crystalline solid—aniline silicofluoride—which forms in the liquid may be digested with a solution of caustic soda in absolute alcohol and sodium silicofluoride will be formed.   See also P. E. Browning, *Amer. J. Science*, (4), 32, 249, 1911; E. Rupp, *Zeit. Nahr. Genuss.*, 22, 496, 1911; A. Sartori, *Chem. Ztg.*, 36, 229, 1912; A. Kickton and W. Behncke, *Zeit. Nahr. Genuss.*, 20, 193, 1910; J. A. Reich, *Chem. Ztg.*, 20, 985, 1896; W. Geilmann, *Glastech. Ber.*, 9, 274, 1931; J. and R. Casares, *Anal. Fis. Quim.*, 28, 910, 1159, 1930.

[2] J. H. de Boer, *Chem. Weekb.*, 21, 404, 1924; *Rec. Trav. chim.*, 44, 1071, 1925; I. Stone, *Journ. Chem. Educn.*, 8, 347, 1931; B. Koone, *Chemist-Analyst*, 20, No. 4, 14, 1931; I. M. Korenman, *Zeit. anorg. allgem. Chem.*, 216, 33, 1933; R. Charonnet, *Compt. rend.*, 199, 1620, 1934.   For the detection of fluorine by mercuric succinimide and benzidine, see C. F. Miller, *Chemist-Analyst*, 26, 35, 1937.

[3] F. Pavelka, *Mikrochem.*, 6, 149, 1928.

[4] I. P. Alimarin, *Zeit. anal. Chem.*, 81, 8, 1930.

[5] Mix 3 volumes of 0·4 per cent. zirconium nitrate solution with 2 volumes of a 0·4 per cent. alcoholic solution of alizarin.

[6] I. M. Kolthoff and M. E. Stanby, *Ind. Eng. Chem. Anal. Ed.*, 6, 118, 1934.

used (fig. 154). It is closed by a ground glass cap carrying an inlet tube extending to the bottom of the flask and an exit tube the open end of which is sealed into a small test tube. The apparatus must be quite dry before use. The dry sample is placed in the flask, together with about 1 grm. of powdered quartz and 25 c.c. of concentrated sulphuric acid. 1 c.c. of purpurin-zirconium reagent [1] is put into the small test tube. A current of air, dried by concentrated sulphuric acid, is passed through the flask, which is heated to 140°–150°, *but no higher*, in an oil bath. With decreasing quantities of fluorine, the reagent becomes yellow with increasing periods of heating as follows:—

FIG. 154.—Kolthoff and Stanby's Apparatus.

Fluorine, mgrms. .	1·0	0·1	0·05	0·03	0·01	0·005
Time, mins. .	0·33	1	3	5	20	40

§ 345. The Gravimetric Determination of Fluorine as Calcium Fluoride.

The fluorides in many silicates are not decomposed by digestion with sulphuric acid and, in consequence, it is necessary to get such fluorides into solution before the analysis can be made. When much fluorine is present the silica must be determined by a special process, because part will be volatilised as silicon tetrafluoride when the aqueous extract of the sodium carbonate fusion is evaporated to dryness.
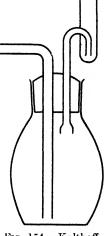
According to Deville and Fouque,[2] the loss on ignition can be determined without losing fluorine, since the decomposition of the calcium fluoride requires a higher temperature than for the expulsion of water.[3] Alkali fluorides, however, volatilise at a comparatively low temperature. Thus, 0·549 grm. of sodium fluoride lost 0·4 per cent. in weight when heated for about 6 minutes in the full flame of a Bunsen burner and 0·2714 grm. lost 1·4 per cent. in weight under the same conditions, while no appreciable loss could be detected after heating 15 minutes with the flame just sufficient to redden the bottom of the platinum crucible.[4]

The methods for the isolation of the fluorides are rather tedious.[5] That commonly used is based upon one proposed by Berzelius and Rose.[6] The

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[1] PURPURIN-ZIRCONIUM REAGENT.—Dissolve 0·16 grm. of zirconium oxychloride in 100 c.c. of concentrated hydrochloric acid and dilute with an equal volume of water. Now dissolve 0·009 grm. of purpurin (1 : 2 : 4-trihydroxyanthraquinone) in 30 c.c. of ethyl alcohol and add this solution slowly to the zirconium oxychloride solution (not *vice versa*). Add to the mixture a further 620 c.c. of concentrated hydrochloric acid and dilute to 1000 c.c. Stand overnight before use; the solution will keep for about a month.

[2] H. St C. Deville and F. Fouque, *Compt. rend.*, 38, 317, 1854. See footnote 6, page 727.

[3] If there is any danger of loss of fluorine during ignition, G. Tammann (*Zeit. anal. Chem.*, 24, 343, 1885) recommends adding a large excess of sodium carbonate or barium hydroxide.

[4] S. Waldbott, *Journ. Amer. Chem. Soc.*, 16, 418, 1894.

[5] For a review of methods for the determination of fluorine, see M. Frommes, *Zeit. anal. Chem.*, 96, 211, 1934; 99, 301, 1934; C. R. Wagner and W. H. Ross, *Journ. Ind. Eng. Chem.*, 9, 1116, 1917.

[6] J. J. Berzelius, *Pogg. Ann.*, 1, 169, 1824; H. Rose, *ib.*, 79, 112, 1850; T. M. Chatard, *Trans. Amer. Inst. Min. Eng.*, 21, 170, 1892–3; F. Wyatt, *The Phosphates of America*, New York, 149, 1892; T. Korovaeff, *Journ. prakt. Chem.*, (1), 85, 442, 1862; P. Jannasch, *Neues Jahr. Min.*, 2, 123, 1883; A. A. Koch, *Journ. Amer. Chem. Soc.*, 29, 1126, 1907; W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, 700, 222, 1919; L. Fricke, *Stahl Eisen*, 24, 889, 1904; E. Zdarck, *Zeit. physiol. Chem.*, 69, 127, 1910; K. Daniel, *Zeit. anorg. Chem.*, 38, 257, 1904;

compound is decomposed by fusion with alkali carbonate—with or without silica. Silica and the bases are precipitated from the solution of the fused cake with ammonium carbonate, ammoniacal zinc oxide (Berzelius' solution) or ammoniacal mercuric oxide (Seemann's solution) and from the resulting solution, calcium or barium fluoride, together with the oxalate, sulphate or carbonate, are precipitated. In the latter case the carbonate is removed by acetic acid and calcium fluoride remains.[1]

The First Silica Precipitation.—Two grams of the uncalcined silicate are fused in a platinum crucible with about 12 grms. of sodium carbonate [2] without the blast.[3] The resulting cake is leached with water, filtered (filtrate A) and washed. Some of the silica, sodium zirconate, barium and calcium carbonates, if present, remain on the filter-paper.[4] The insoluble residue is rinsed into a basin and boiled for a few minutes with 50 c.c. of 5 per cent. sodium carbonate solution to extract the remainder of the fluorine from it. The residue is again filtered off and washed free from alkali with hot water. The filtrate is added to filtrate A. A hole is poked through the filter-paper and the residue [5] washed into an evaporating basin with hot 10 per cent. hydrochloric acid. The paper is washed free from chlorides and is reserved, together with the acid solution (solution X), for the determination of silica and bases.

The Second Silica Precipitation.—Filtrate A and washings contain the fluorine as alkali fluoride, the remainder of the silica and also alumina, if present. Introduce 10 grms. of solid ammonium carbonate and digest the mixture for about 12 hours at about 40° to 50°, whereby the alumina and a further quantity of the silica are precipitated.[6] Filter and wash the precipitate with aqueous ammonium carbonate. The filtrate (filtrate B) still contains some silica. The precipitate is dissolved off the paper with hot hydrochloric acid solution and the paper washed free from chlorides. The paper is retained and the acid solution and washings are added to solution X.

The Third Silica Precipitation.—Evaporate filtrate B to dryness [7] on a water bath; digest the residue with a little water and cool. Add two drops

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F. P. Treadwell and A. A. Koch, *Zeit. anal. Chem.*, **43**, 469, 1904; W. H. Adolph, *Journ. Amer. Chem. Soc.*, **37**, 2500, 1915; P. Urech, *Chem. Ztg.*, **86**, 855, 1933; L. Graber, *Ing. chim.*, **17**, 123, 1929; M. Karasinski, *Bull. intern. Acad. Polonaise*, **2A**, 143, 1931; *Ann. Rep. Progress. Chem.*, **23**, 196, 1927; G. A. Shuey, *Journ. Assoc. Off. Agr. Chem.*, **11**, 147, 1928; P. Deceuleneer, *Ing. chim.*, **18**, 78, 1934.

[1] Small amounts of fluorine can be determined colorimetrically with advantage—page 735.

[2] Calcium fluoride cannot be completely decomposed by fusion with sodium carbonate, but the decomposition is complete if the fluoride be mixed with silica or a silicate, whereby a double sodium calcium silicate is formed. To avoid frothing, the silica and sodium carbonate may be fused beforehand—P. Fuchs, *Chem. Erde*, **5**, 99, 1930. Hence, if the fluorides be high and the silica low, the addition of 3 grms. of silica is recommended to ensure complete decomposition (page 740). This is not usually needed for Cornish stone, nor for glazes.

[3] G. Forchhammer stated that all the fluorine is not obtained by melting silicates, *e.g.* topaz or tourmaline, with sodium carbonate; and Städeler states that if the lid be removed during the fusion there will be a loss of fluorine (*Journ. prakt. Chem.*, (1), **99**, 66, 1866).

[4] If sulphur and chlorine are to be determined, the solution from the fused cake can be made up to 250 c.c. Take 50 c.c. for the sulphur, 100 c.c. for the fluorine and 100 c.c. for the chlorine. But the solutions may be so dilute that it may be advisable to use a separate sample for these determinations rather than take a correspondingly greater amount of the original sample for this fusion.

[5] W. H. Adolph (*Journ. Amer. Chem. Soc.*, **37**, 2500, 1915) recommends a second fusion of the residue to extract the last traces of fluorine from it.

[6] J. I. Hoffman and G. E. F. Lundell (*Bur. Standards Journ. Research*, **3**, 581, 1929) say that the precipitation of silica at this stage is aided by adding a nitric acid solution of zinc nitrate until the concentration of sodium carbonate has been reduced to about 1 per cent.

[7] The liquid is inclined to froth and spit during the evaporation. Hence, the dish must be covered by a clock-glass until all the ammonium carbonate has been decomposed. Then remove the clock-glass and rinse its under side into the basin.

of methyl red indicator and run in from a burette 2N-nitric acid until the indicator begins to change colour. Boil off the dissolved carbon dioxide and cool; now add more nitric acid until, on heating, the yellow colour of the indicator does not return. Add, say, 5 c.c. of Seemann's solution [1] and evaporate the mixture until the smell of ammonia has disappeared. The precipitate, consisting of traces of silica and mercuric oxide,[2] is filtered off (filtrate C) and washed with water. The precipitate and filter-paper are retained.

The Precipitation of the Fluoride as Calcium Fluoride.—Add nitric acid to filtrate C and washings until the alkali carbonate is nearly decomposed. If too much acid be run in, a little more sodium carbonate must be added, so that the solution is distinctly alkaline. Boil with a large excess of an aqueous solution of calcium chloride.[3] Calcium carbonate and fluoride are precipitated.[4]

The Removal of Calcium Carbonate.—Collect the precipitate on a filter-paper,[5] wash with hot water, dry and ignite slowly to faint redness,[6] in a platinum basin.[7] Cover the basin with a clock-glass and introduce through

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[1] SEEMANN'S SOLUTION.—Mercuric oxide is precipitated by adding an aqueous solution of sodium hydroxide to a hot saturated solution of mercuric chloride. The precipitate is washed with hot water until a portion of it volatilises on platinum foil without residue. About 20 grms. of moist mercuric oxide, freshly prepared as above, is dissolved to saturation in a litre of Schaffgotsch's solution, made by dissolving 230 grms. of ammonium carbonate in 180 c.c. of ammonia solution (sp. gr. 0·92) and diluting to 1000 c.c.—F. Seemann, *Zeit. anal Chem.*, 44, 343, 1905.

BERZELIUS' SOLUTION.—A solution of ammonio-zinc oxide, as originally recommended by J. J. Berzelius (*l.c.*), is sometimes used instead. Precipitate an aqueous solution of pure zinc sulphate with caustic potash. Filter, wash by decantation and dissolve the precipitate in ammonia—M. Kleinstück, *Zeit. anal. Chem.*, 50, 697, 1911; J. I. Hoffman and G. E. F. Lundell, *Bur. Standards Journ. Research*, 3, 581, 1929.

[2] And phosphate, if all was not precipitated with the alumina. Test with a solution of ammonium molybdate. If phosphorus be present, add an excess of silver nitrate solution. This precipitates silver phosphate and carbonate. Warm the solution in order to coagulate the precipitate and filter. Precipitate the excess of silver nitrate with an aqueous solution of sodium chloride (2E). Boil the solution to coagulate the silver chloride and filter. Add a little sodium carbonate until the solution reacts alkaline. The same procedure removes any chromate as silver chromate—W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, 700, 223, 1919.

[3] CALCIUM CHLORIDE SOLUTION.—Dissolve 21·9 grms. of the crystalline salt ($CaCl_2 . 6H_2O$) in 100 c.c. of water (2E).

[4] G. Starck and E. Thorin (*Zeit. anal. Chem.*, 51, 14, 1912) add a known amount of oxalic acid and precipitate the fluorine with calcium oxalate by the addition of calcium chloride in a solution slightly acidified with acetic acid. The precipitate is filtered on asbestos, dried at 210° and weighed. The calculated amount of calcium oxalate is deduced and the difference represents calcium fluoride. See also W. W. Scott, *Ind. Eng. Chem.*, 16, 703, 1924; F. A. Gooch and M. Kobayashi, *Amer. Journ. Sci.*, (4), 45, 370, 1918.

[5] Calcium fluoride alone gives a slimy precipitate which is very difficult to filter, but in the presence of calcium oxalate or carbonate it filters better. G. G. Kandilarow (*Ber.*, 61B, 1667, 1928) recommends the use of membrane filters; P. Mougnaud (*Compt. rend.*, 194, 1507, 1932) finds that calcium fluoride can be washed completely and rapidly by centrifuging, and S. G. Clarke and W. N. Bradshaw (*Analyst*, 57, 138, 1932) say that calcium fluoride can be precipitated and filtered without difficulty, even in the absence of co-precipitates, if an excess of calcium chloride and filter-paper pulp be used.

[6] A slight loss of fluorine may occur by ignition of the filter-paper in contact with calcium fluoride. G. Tammann, *Zeit. anal. Chem.*, 24, 328, 1885; W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, 700, 225, 1919. W. Hempel (*Gasanalytische Methoden*, Braunschweig, 347, 1900) found that 1·5 grms. heated 15 minutes at 1000° lost 0·019 grm.; and at a dull red heat, 0·005 grm. F. Seemann (*Zeit. anal. Chem.*, 44, 343, 1905) noticed a loss of 0·0008 grm. when a gram was heated over a Teclu's burner at 1000°; and F. P. Treadwell and A. A. Koch (*Zeit. anal. Chem.*, 43, 469, 1904) found a loss of 0·0002 grm. after ignition for 10 minutes over a Teclu's burner, and 0·0009 grm. after half an hour's heating. P. Mougnaud (*Compt. rend.*, 192, 1733, 1931) says that calcium fluoride is stable in a covered crucible up to 800°.

[7] Instead of carrying this process any further, we may proceed to § 348, page 731.

a pipette, dilute acetic acid [1] in excess of that needed to dissolve the calcium carbonate. Heat the covered basin on a water bath until effervescence ceases, then remove the clock-glass, rinse its under side into the basin and evaporate to dryness. Digest the residue in water very slightly acidulated with acetic acid.[2] Filter and wash as before, the filtrate being retained. The digestion with the weak acetic acid solution may be repeated, particularly if much fluorine be present, to ensure that the last traces of soluble calcium compounds have been removed; the filtrate is again retained.[3] The complete removal of calcium oxide and carbonate is shown by the absence of residue when a drop or two of the filtrate is evaporated to dryness on a piece of platinum foil. The last filter-paper containing the precipitated calcium fluoride is ignited gently to faint redness in a platinum crucible—this temperature just suffices to burn off the filter-paper—the crucible and contents are then weighed.

Owing to the solubility of calcium fluoride in acetic acid and to the possible loss of hydrofluoric acid when calcium fluoride is evaporated in contact with acetic acid, the following modification has been proposed [4]:—The solution of the alkali fluoride, after neutralisation with nitric acid, is made slightly ammoniacal and then calcium fluoride is precipitated by the addition of an excess of an aqueous solution of calcium chloride. The precipitate is filtered off [5] and washed with a hot aqueous solution of ammonia until free from chlorides.

Verification of the Result.— That the precipitate is really calcium fluoride should be confirmed by converting the calcium fluoride into calcium sulphate by the addition, drop by drop, of concentrated sulphuric acid. Drive off the excess of acid by evaporation and test the fumes for hydrogen fluoride by means of a greased glass plate in the usual manner. Gradually raise the temperature to a red heat. Cool and weigh. One gram of CaF_2 should give 1·7436 grms. $CaSO_4$. If the weights are not concordant, as they rarely are, the impurity may be silica, calcium silicate or calcium phosphate arising from the imperfect separation of silica and phosphorus, or it may be calcium sulphate which has not been washed out of the precipitate. Phosphates can be detected by the molybdate reaction in the hot nitric acid solution of the precipitate, but it is not easy to decide whether the impurity be calcium silicate or silica. If phosphate and silicate be present, these may be de-

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[1] If the precipitate were treated directly with the acetic acid, without the preliminary ignition, the proper washing of the fluoride would be extremely difficult.

[2] S. L. Penfield and J. C. Minor, *Amer. J. Science*, (3), **47**, 389, 1894; W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, **700**, 225, 1919; F. P. Treadwell and A. A. Koch, *Zeit. anal. Chem.*, **43**, 469, 1904; O. Kallauner and K. Kuraš, *Zprávy Československ. Keram. Spole.*, **11**, 24, 1934; *Chem. Zentr.*, (2), 2865, 1935. According to Treadwell and Koch (*l.c.*), the loss of calcium fluoride per 100 c.c. of wash-water is about 0·0015 grm. With a one-gram sample, therefore, from 0·04–0·05 per cent. of fluorine will entirely escape observation—W. F. Hillebrand (*l.c.*). For the solubility of calcium fluoride in water and in acetic acid, see also P. Mougnaud, *Compt. rend.*, **192**, 1733, 1931; L. Dupare, P. Wenger and G. Graz, *Helv. Chim. Acta*, **8**, 280, 1925. Calcium fluoride is not attacked by lactic, butyric, tartaric, citric, formic, salicylic or benzoic acid; the alkali fluorides are—P. A. E. Richards, *Analyst*, **39**, 248, 1914. For the colloidal properties of calcium fluoride, see E. Paterno and E. Mazzucchelli, *Atti R. Accad. Lincei*, **12**, ii, 420, 520, 1903.

[3] Since the last traces of silica may have escaped precipitation, these two filtrates are combined and the silica in them determined by evaporation to dryness with hydrochloric acid. The weight of the silica thus obtained is added to the weight of that separated from solution X.

[4] E. Carrière and Rouanet, *Compt. rend.*, **189**, 1281, 1929; E. Carrière and Janssens, *ib.*, **190**, 1127, 1930; **193**, 490, 1931; *cf.* S. G. Clarke and W. N. Bradshaw, *Analyst*, **57**, 138, 1932; P. Mougnaud, *Compt. rend.*, **194**, 1507, 1932; D. J. Pflaum and H. H. Wenzke, *Ind. Eng. Chem. Anal. Ed.*, **4**, 392, 1932; F. L. Hahn, *Zeit. anal. Chem.*, **69**, 385, 1926.

[5] See footnote 5, page 727.

composed by the sulphuric acid treatment, but if the impurity is silica or calcium sulphate no decomposition will result and it is possible to calculate the amount of calcium fluoride from the observed increase in weight. From the equation

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF$$

an increase in weight of 58·06 grms. corresponds to the conversion of 78·08 grms. of calcium fluoride into 136·14 grms. of calcium sulphate. Hence an increase in weight of w grms., obtained by the action of sulphuric acid on the sample, represents 1·3448w grm. of calcium fluoride or 0·65453w grm. of fluorine. In illustration,

Calcium fluoride (found)	.	.	.	0·0426 grm.
Calcium sulphate (found)	.	.	.	0·0724 grm.
Calcium sulphate (theory)	.	.	.	0·0743 grm.

No phosphates or silicates were present. Hence, it is assumed that the impurity was calcium sulphate not perfectly washed away. Consequently, the amount of fluorine in the 2 grm. sample is 0·65453 × (0·0724 − 0·0426) = 0·0195 grm. Hence, the sample has 0·975 per cent. of fluorine; or, 2·00 per cent. of calcium fluoride.

Errors.—Owing to the relatively small amounts of fluorine usually present in natural silicates, great care must be taken to prevent, as far as possible, any contamination of the calcium fluoride. The chief sources of error are: (1) loss of fluorides owing to adsorption by the voluminous "silica" precipitates[1]; (2) the solubility of calcium fluoride in water and acetic acid; (3) loss of calcium fluoride by volatilisation, particularly in contact with the filter-papers; and (4) the contamination of the precipitated calcium fluoride with phosphates, silica, calcium silicate or calcium sulphate.

Correction of the Analysis "Total" for Fluorine.—In summing up the results of a silicate analysis which includes appreciable amounts of fluorine or chlorine, the sum of the constituents will exceed the limit "100 ± 0·5." This is due to the fact that the bases have been calculated as oxides when some of the bases were really present as fluorides or silicofluorides. For instance, a translucent white glass gave on analysis[2]:

SiO$_2$	Al$_2$O$_3$	MnO	ZnO	MgO	CaO	Na$_2$O	F
64·8	9·3	1·1	7·0	0·2	1·9	10·8	8·1

The total reaches 103·2. But 38 grms. of fluorine are equivalent to 16 grms. of oxygen, or 1 grm. of fluorine is equivalent to 0·42105 grm. of oxygen. Consequently 8·1 grms. of fluorine are equivalent to 8·1 × 0·421 = 3·4 grms. of oxygen. Hence, we append to the statement: "Total, 103·2," "less 3·4 per cent. of oxygen, corresponding with 8·1 per cent. of fluorine."

§ 346. Determination of Fluorine as Lead Chlorofluoride. Starck's Process.

In 1911 Starck proposed to determine fluorine by precipitation as lead chlorofluoride,[3] PbClF. This salt has a solubility in water of 0·325 grm. per

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[1] Hence, some recommend collecting the different "silica" precipitates, igniting and again fusing the residue with sodium carbonate. See footnote 5, page 726.

[2] "Alumina" in the analysis includes ferric oxide.

[3] G. Starck, *Zeit. anorg. Chem.*, **70**, 173, 1911; W. H. Adolph, *Journ. Amer. Chem. Soc.*, **37**, 2500, 1915; L. D. Hammond, *Ind. Eng. Chem.*, **16**, 938, 1924; F. G. Hawley, *ib.*, **18**, 573, 1926; D. S. Reynolds and K. D. Jacob, *ib.*, *Anal. Ed.*, **3**, 366, 1931; J. I. Hoffman and

litre; its solubility is increased in the presence of hydrochloric and acetic acids, but it is almost insoluble in dilute solutions of lead chloride.

Filtrate C and washings, obtained as described in §345, are used for the determination.[1]   Various procedures have been recommended; that adopted by Hoffman and Lundell, with slight modification, is as follows:—Dilute the solution to 250 c.c., add 3 c.c. of a 10 per cent. solution of sodium chloride and two drops of bromophenol blue indicator.   Run dilute nitric acid into the solution until its colour changes to yellow.   Heat to boiling to expel carbon dioxide, cool and then add dilute sodium hydroxide solution until the colour changes to blue.   Now add 2 c.c. of hydrochloric acid (1 : 1) and 5 grms. of pure lead nitrate.   Heat the mixture on a water bath until the lead nitrate has dissolved, then add 5 grms. of pure crystalline sodium acetate.   Stir well, digest on a water bath for 30 minutes with occasional stirring and stand overnight in the cold.

Gravimetric Determination.—The solution is filtered through a Gooch crucible which has been dried at 150° and weighed. The precipitate is transferred to the crucible, washed four or five times with a cold saturated solution of lead chlorofluoride [2] and finally washed with a little cold water. The crucible and contents are dried for 2 hours at 150° and again weighed. Lead chlorofluoride contains 7·261 per cent. of fluorine.[3]

Volumetric Determination.—The solution is filtered through a fine grade gravimetric paper and the precipitate washed as above. The paper and precipitate are transferred to the beaker in which the precipitation was made and digested with 100 c.c. of 5 per cent. nitric acid until the precipitate has dissolved and the paper has been reduced to pulp. A measured excess of 0·2N-silver nitrate solution is added and the mixture digested for 30 minutes on a water bath. After cooling in the dark to room temperature, filter, wash and determine the silver in the filtrate by Volhard's process, page 65. Each c.c. of 0·2N-silver nitrate used in reacting with the lead chlorofluoride represents 0·0038 grm. of fluorine.

Errors.—If the original solution contains sulphates, chromates or phosphates, or carbonates, due to the incomplete expulsion of carbon dioxide, the corresponding lead salts will be wholly or partially precipitated with the lead chlorofluoride. In these circumstances the gravimetric process will be vitiated but, unless these precipitates carry down chlorides with them, they will have no harmful effect in small amounts on the volumetric process.

G. E. F. Lundell, *U.S. Bur. Standards Journ. Research*, **3**, 581, 1929; I. Tananaev, *Zeit. anal. Chem.*, **99**, 21, 1934; A. A. Vasil'ev, *Journ. App. Chem. (U.S.S.R.)*, **9**, 747, 943, 1936; F. Specht, *Zeit. anorg. allgem. Chem.*, **231**, 181, 1937. The process has been adversely reported on by S. G. Clarke and W. N. Bradshaw, *Analyst*, **57**, 138, 1932; J. Fischer and H. Peisker, *Zeit. anal. Chem.*, **95**, 225, 1933; F. J. Frere, *Ind. Eng. Chem. Anal. Ed.*, **5**, 17, 1933.

[1] The solution should contain, preferably, from 0·01 to 0·1 grm. of fluorine. If more than about 10 grms. of sodium salts are present the results tend to be low.

[2] Make two solutions as follows:—(1) 10 grms. of lead nitrate in 200 c.c. of water, and (2) 1 grm. of sodium fluoride in 100 c.c. of water and 2 c.c. of concentrated hydrochloric acid. Mix the two solutions, allow the precipitate to settle and wash it by decantation four or five times with 200 c.c. of water. Add to the precipitate 1 litre of cold water and stand for 1 hour, with occasional shaking. Filter and use the filtrate. The residue can be used for preparing fresh supplies of wash liquor.

[3] For the gravimetric determination of fluorine as thorium fluoride, see E. Deladier, *Chem. Weekb.*, **1**, 324, 1904; *Chem. Zentr.*, (2), 1104, 1904; F. Pisani, *Compt. rend.*, **162**, 791, 1916; F. A. Gooch and M. Kobayashi, *Amer. Journ. Sci.*, (4), **45**, 370, 1918; as lanthanum fluoride, R. J. Meyer and W. Schutz, *Zeit. angew. Chem.*, **38**, 203, 1925; A. Mayerhofer, C. Schneider and A. Wasitzky, *Biochem. Zeit.*, **251**, 70, 1932; as triphenyl tin fluoride, N. Allen and N. H. Furman, *Journ. Amer. Chem. Soc.*, **54**, 4625, 1932.

§ 347. The Determination of Silica in the Presence of Fluorides.

For reasons stated on page 151, the silica cannot be properly determined by the method of page 147 when fluorides are present, but it can be determined in the by-products of the fluorine determination, namely, the three precipitates indicated on pages 726 and 727. The three filter-papers, obtained in the silica separations, are ignited in a platinum crucible and the ashes added to solution X. 10 c.c. of concentrated hydrochloric acid are added and the solution evaporated to dryness on a water bath. The silica is recovered in the usual way. The mercury volatilises on ignition. The alumina, titanic oxide, ferric oxide, magnesia and lime [1] can be determined separately in another portion of the silicate decomposed by the hydrofluoric acid treatment, or in the filtrate from the silica.[2]

Schrenk and Ode [3] have shown that silica can be accurately determined in the presence of fluorspar as follows: Half a gram of the finely ground sample is digested in a hard glass beaker with 15 c.c. of 20 per cent. perchloric acid, previously saturated with boric acid at 50°, until fumes of perchloric acid have been evolved for 5 minutes. A few c.c. of water are added and the fuming repeated for another 5 minutes. 75 c.c. of water are then added, the solution heated and the insoluble residue filtered off. The residue and filter-paper are washed with dilute perchloric acid and finally with hot water until the washings give no precipitate with ammonium oxalate. The insoluble residue is ignited and the silica in it determined by the loss in weight after evaporation with hydrofluoric acid.

§ 348. The Gravimetric Determination of Fluorine as Potassium Fluosilicate.

In Carnot's process [4] for the determination of fluoride, the silicate is digested with sulphuric acid, and the silicon tetrafluoride is passed into an aqueous

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[1] In glazes, the lead, tin, etc., can be conveniently determined in a portion decomposed with sulphuric and hydrofluoric acids.

[2] H. Gilbert, *Corresp. Ver. anal. Chem.*, 3, 1, 1880. For the determination of silica in the presence of fluorine and in fluorine minerals, see R. Fresenius and E. Hintz, *Zeit. anal. Chem.*, 28, 324, 1889; J. Loczka, *ib.*, 49, 328, 1910; W. F. Hillebrand, *Bull. U.S. Geol. Survey*, 700, 226, 1919; A. Stadeler, *Stahl Eisen*, 47, 662, 1927; H. Dubiel, *Oester. Chem. Ztg.*, 29, 174, 1926; J. I. Hoffman and G. E. F. Lundell, *Bur. Standards Journ. Research*, 3, 581, 1929; W. L. Hill and K. D. Jacob, *Journ. Assoc. Official Agr. Chem.*, 13, 112, 1930; K. M. Timofeyuk, *Zavodskaya Lab.*, 3, 19, 1933. Compare A. Travers, *Compt. rend.*, 185, 893, 1927.

[3] W. T. Schrenk and W. H. Ode, *Ind. Eng. Chem. Anal. Ed.*, 1, 201, 1929. F. Specht (*Zeit. anorg. allgem. Chem.*, 231, 181, 1937) fuses up with boric acid to expel hydrofluoric acid, extracts the melt with water and removes excess of boric acid by evaporation below the boiling-point, after adding a solution of methyl chloride in methyl alcohol.

[4] A. Carnot, *Ann. Mines*, (9), 3, 138, 1893; *Compt. rend.*, 114, 750, 1892; *Bull. Soc. chim.*, (3), 9, 71, 1893; H. Lasne, *ib.*, (2), 50, 167, 1888; *Ann. Chim. anal.*, 2, 161, 182, 1897; E. Coutal, *ib.*, 2, 401, 1897; A. Liversidge, *Chem. News*, 24, 226, 1871; G. Harker, *ib.*, 82, 56, 64, 1900; J. Schuch, *Zeit. Landw. Vers. Öst.*, 9, 531, 1904; A. Küpffer, *Archiv Nat. Liv. Est. Kurlands*, (1), 5, 114, 1874; W. E. Burk, *Journ. Amer. Chem. Soc.*, 23, 825, 1901; P. Jannasch and A. Röntgen, *Zeit. anorg. Chem.*, 9, 267, 1895; K. Daniel, *ib.*, 38, 257, 1904; A. Hilemann, *ib.*, 51, 162, 1906; J. M. van Bemmelen, *ib.*, 15, 84, 1897; F. Bullnheimer, *Zeit. angew. Chem.*, 14, 101, 1901; E. Prost and F. Balthaser, *ib.*, 14, 292, 1901; *Bull. Assoc. Belg. Chim.*, 13, 453, 1899; H. von Kobell, *Journ. prakt. Chem.*, (1), 92, 385, 1864; F. Stolba, *ib.*, (1), 89, 129, 1863; F. Wöhler, *Pogg. Ann.*, 48, 87, 1839; J. Brandl, *Liebig's Ann.*, 213, 1, 1882; H. Schiff, *Liebig's Ann. Suppl.*, 4, 27, 1865; R. Fresenius, *Anleitung zur quantitativen chemischen Analyse*, Braunschweig, 1, 431, 1875; *Zeit. anal. Chem.*, 5, 190, 1866; S. Bein, *ib.*, 26, 733, 1887; E. Wrampelmeyer, *ib.*, 32, 550, 1893; J. Casares, *ib.*, 34, 546, 1895; 44, 729, 1905; *Anal. Fis. Quim.*, 27, 290, 1929; A. Gautier and P. Clausmann, *Compt.*

solution of potassium fluoride, and finally weighed as potassium fluosilicate. Carnot's process is thus based upon older methods by Fresenius, and by Wöhler. The method gives good results with many of the natural fluorides used industrially, and also with slags and frits. All these are supposed to be decomposed by hot concentrated sulphuric acid.[1] Daniel considers that methods depending on the volatilisation of silicon tetrafluoride are not reliable if amorphous silica, or silicates, be present, because a non-volatile fluoride may be formed which leads to low results.[2] On the other hand, Classen[3] actually recommends: "One part of powdered quartz and 0·5 part of *precipitated silica* is to be intimately mixed in an agate mortar with the substance to be analysed." If there be any reason to suspect low results from the cause indicated by Daniel, the silicate can be treated as described in the preceding section. When all the silica has been separated, and the precipitate containing calcium fluoride and carbonate has been ignited, the mixture, if desired, can be treated by Carnot's process as follows.

The Preparation of the Substance for Analysis.—2 grams of the finely ground substance under investigation are mixed with twice their own weight of finely ground, dry, quartz sand,[4] or rock crystal. If the sample contains other than about 0·1 grm. of fluorine, a proportionally less or greater amount than 2 grms. may be taken.[5]

Fitting-up the Apparatus.[6]—The mixture is placed in an Erlenmeyer's flask of about 150 or 250 c.c. capacity (*A*, fig. 155). The flask is closed with a three-hole rubber stopper and connected with the system shown in the diagram. A Walter's gas-washing bottle[7] *C*, charged with concentrated sulphuric acid, is also fitted with a tube *B*, charged with soda lime. The former is connected with the flask containing the substance under investigation by means of a tube extending to the bottom of the Erlenmeyer's flask, *A*. The flask *A* is fitted with a stoppered funnel *D* and is also connected to an Emmerling's or similar drying tube *E*, packed with glass beads, in order to

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rend., 154, 1469, 1912; H. A. Weber, *Centr. Min.*, 2, 504, 1902; J. Tananaev, *Journ. App. Chem.* (*U.S.S.R.*), 5, 834, 1932; N. I. Sinitzuin and V. G. Feigman, *ib.*, 8, 152, 1935; P. Deceulenecr, *Ing. chim.*, 18, 78, 1934; D. S. Reynolds, W. H. Ross and K. D. Jacob, *Journ. Assoc. Official Agr. Chem.*, 11, 225, 1928; W. D. Armstrong, *Ind. Eng. Chem. Anal. Ed.*, 5, 315, 1933; G. R. Sharpless and E. V. McCollum, *Journ. Nutrition*, 6, 163, 1933.

[1] For perchloric acid, see H. H. Willard and O. B. Winter, *Ind. Eng. Chem. Anal. Ed.*, 5, 8, 1933.

[2] K. Daniel (*l.c.*); D. S. Reynolds and K. D. Jacob (*Ind. Eng. Chem. Anal. Ed.*, 3, 371, 1931) also condemn silica gel and the presence of silicates decomposable by sulphuric acid. They recommend quartz. See also S. N. Rozanov and V. A. Kazarinova, *Trans. Sci. Inst. Fertilisers* (Moscow), 113, 96, 1933; S. N. Rozanov, *Zavodskaya Lab.*, 3, 791, 1934; L. Szegö and B. Cassoni, *Giorn. Chim. Ind. Appl.*, 15, 599, 1933. H. Herlemont and J. Delabre (*Compt. rend.*, 196, 1502, 1933) say that the use of ferrosilicon with 75 per cent. of silicon gives much better results than quartz.

[3] A. Classen, *Ausgewählte Methoden der analytischen Chemie*, Braunschweig, 2, 430, 1903.

[4] The quartz sand should be moistened with sulphuric acid, and calcined to remove organic matter, or treated by Hempel's process of purification (footnote 1, page 740).

[5] For example, 0·2 grm. of fluorspar or cryolite will suffice; 2 grms. of mineral phosphates containing from 2 to 3 per cent. of fluorine; and 5 grms. of bone ash with about 0·2 per cent. of fluorine can be taken for the analysis. If the silica and alumina are not to be determined, the preliminary treatment with Seemann's solution may not be needed. The ammonia must, however, be eliminated. If the fluorides are completely decomposed by sulphuric acid, the treatment with sodium carbonate may be omitted if the silica is not to be determined.

[6] For alternative forms of distillation apparatus, see D. S. Reynolds, W. H. Ross and K. D. Jacob, *Journ. Assoc. Official Agr. Chem.*, 11, 225, 1928; W. F. Hillebrand and G. E. F. Lundell, *Applied Inorganic Analysis*, New York, 599, 1929. W. D. Armstrong (*Ind. Eng. Chem. Anal. Ed.*, 5, 315, 1933) has evolved an apparatus in which all gas-scrubbing devices are eliminated, the fluorine being determined colorimetrically.

[7] J. Walter, *Dingler's Journ.*, 251, 367, 1884.

remove any acid vapours which might rise from the flask. The Emmerling's tube is in turn connected with a tube F, drawn out at one end. This dips 2 or 3 mm. beneath the surface of 10 c.c. of mercury contained in a small cylindrical vessel closed by a two-hole rubber stopper (G, fig. 155). This
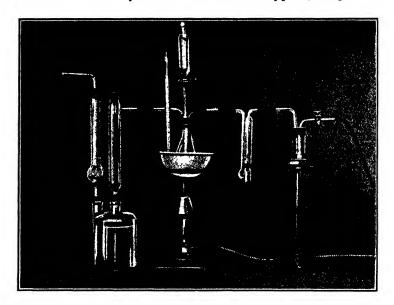
FIG. 155.—The Determination of Fluorine as Potassium Fluosilicate.
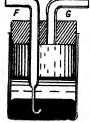
vessel is shown enlarged in the sectional diagram, fig. 156. This vessel also contains about 20 c.c. of a neutral solution of potassium fluoride [1]—20-25 per cent.

The utmost care must be taken that all the glass parts between B and G be thoroughly dried. Failure to remove the last traces of adsorbed moisture from the walls of the system inevitably leads to low results.[2] The drying is best effected by aspirating a current of dry air through the apparatus while the different parts are warmed.

The Decomposition of the Fluoride.—Add 40 c.c. of 98 to 98·5 per cent. sulphuric acid [3] to the flask A by means of the funnel D. Aspirate a current of air through the system so that about one bubble per second rises through the

FIG. 156.—Absorption Vessel.

[1] POTASSIUM FLUORIDE SOLUTION.—Commercial potassium fluoride is generally acid and attacks glass. To prepare this for the work, dissolve 25 grms. in 80 c.c. of distilled water in a platinum dish; add dilute potash solution, drop by drop, until the solution is neutral to tincture of cochineal. Add absolute alcohol, drop by drop, until the solution shows a faint turbidity. Let the precipitate settle and filter. If the solution is free from potassium fluosilicate, it should give no precipitate when 10 c.c. is mixed with 40 c.c. of water and 50 c.c. alcohol (90 per cent.).

[2] O. Kallauner and K. Kuráš (*Stavivo*, 65, 1933) add dehydrated copper uranate to the contents of the decomposition flask to ensure complete retention of any water formed during the reaction.

[3] The sulphuric acid should be free from oxides of nitrogen, hydrochloric and hydrofluoric acids. This can be effected by heating the acid in a platinum basin along with a little powdered quartz.

mercury in *G*.   The flask *A* is heated in a suitable oil bath, *H*, and the temperature gradually raised to 150° or 160°, as indicated by the thermometer *T*.[1]   The fluorides in *A* begin to decompose at about 100°, and potassium fluosilicate begins to separate in the aqueous solution in *G*.   If any bubbles of the fluosilicate stick to the walls of *G*, they must be broken up by gently rotating the fluid.   When no new bubbles of the fluosilicate are formed, aspirate air a little more vigorously through the system for about half an hour.

The Preparation of the Potassium Fluosilicate for Weighing.—Decant the fluid containing the gelatinous precipitate into an Erlenmeyer's flask; wash the absorption vessel, *G*, and the mercury two or three times with a little distilled water.[2]   The main liquid and the washings are collected in the same flask, the contents of which should not exceed 100 c.c.   Shake the liquid with its own volume of absolute alcohol; let the mixture stand 2-3 hours; decant the clear liquid through a Gooch crucible which has been dried at 100° and weighed; wash the precipitate on to the filter with a mixture of equal volumes of water and alcohol, taking care to leave any globules of mercury in the flask; continue washing until the washings give no precipitate with calcium chloride—30-40 c.c. of the dilute alcohol are usually sufficient.   Dry the Gooch crucible and contents at 100° and weigh.

Weighings.—A half-gram sample of purple Cornish stone, when treated as described above, gave:

Crucible and precipitate	8·4519 grms.
Crucible alone	8·4321 grms.
Potassium fluosilicate	0·0198 grm.

The weight of the potassium fluosilicate, multiplied by 0·5176, gives the corresponding amount of fluorine; and by 1·0635, the corresponding amount of calcium fluoride.   Hence, the sample contained the equivalent of $0.5176 \times 0.0198 = 0.01025$ grm. or 2·05 per cent. of fluorine; or $1.0635 \times 0.0198 = 0.02106$ grm. or 4·21 per cent. of calcium fluoride.

Disturbing Factors.—This method gives more exact results with less trouble in manipulation than by the precipitation process (page 725).   The principal sources of error are: (1) The presence of moisture in the air or in the system through which the silicon tetrafluoride passes.   This causes a decomposition of the silicon fluoride before it reaches the potassium fluoride and thus gives low results.   (2) The passage of sulphuric acid fumes along with the gases from the flask *A*.   This decomposes the potassium fluoride in the receiving vessel and leads to the formation of potassium fluosilicate from the silica in the glass, giving high results.   (3) Incomplete decomposition of the fluoride in the flask *A*.   (4) Failure to sweep all the silicon fluoride from the evolution flask.   (5) Too rapid evolution of gas, which prevents complete absorption of the silicon fluoride.   (6) The action of the potassium fluoride on the glass.   To avoid the latter, Carnot recommends coating the surfaces of the flasks and tubes used in the determination with, say, copal resin.

A blank experiment will soon show whether the reagents and method are trustworthy.   When *chlorides* are present, a U-tube containing pumice

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[1] D. S. Reynolds, W. H. Ross and K. D. Jacob (*Journ. Assoc. Official Agr. Chem.*, **11**, 225, 1928) recommend a temperature of 300° and heat by means of an electric resistance furnace.   W. H. Adolph (*Journ. Amer. Chem. Soc.*, **37**, 2500, 1915) works at a temperature of 200°-220°.

[2] If the glass is attacked the experiment is vitiated.   Some object to the use of the "policeman," since it removes silica from the glass.   The silica is formed by the action of the fluorides.

saturated with anhydrous copper sulphate (page 625) must be interposed between E and F. If the mercury in G has a greenish film towards the end of an experiment, *iodides* are probably present. If so, start a new experiment with a tube of copper turnings interposed, with the object of arresting the iodine. Alternatively, halogens can be removed by passing the gases through a 10 per cent. solution of anhydrous silver sulphate in 98 per cent. sulphuric acid. Sulphur dioxide and oxides of nitrogen are eliminated by washing with a saturated solution of chromium trioxide (previously dried at 110°) in 98 per cent. sulphuric acid. Sulphur trioxide mist is removed by scrubbing the gas through glass wool immediately before its passage into the absorption vessel. If *organic* matter be present, this should be removed by calcination of the weighed sample with half its weight of lime for 1 to 2 hours at 500°–600°.

Offermann's Volumetric Process.—Instead of isolating and weighing the potassium fluosilicate, it is now customary to proceed by Offermann's modification [1] of Carnot's method, in which the silicon tetrafluoride is collected in water. The fluoride is decomposed thus:—

$$3SiF_4 + 4H_2O = 2H_2SiF_6 + Si(OH)_4$$

The hydrofluosilicic acid is then titrated with standard alkali according to the equation:—

$$H_2SiF_6 + 6NaOH = 6NaF + Si(OH)_4 + 2H_2O$$

Hence, after all the silicon fluoride has been evolved, the contents of the absorption vessel are rinsed out into a flask and the solution is diluted to 200–250 c.c. Boil for about 5 minutes and then titrate the *hot* solution with 0·1N- or 0·02N-alkali, using phenolphthalein as indicator. The volume of standard alkali used in a blank run is subtracted from the volume taken in the above titration. From the equation it follows that 1 c.c. of 0·1N-alkali corresponds with 0·0019 grm. of fluorine or 0·0039 grm. of calcium fluoride.

§ 349. The Colorimetric Determination of Fluorine—
I. Steiger's Process.

Steiger [2] has devised a process for the determination of fluorine which is based on the well-known fact that the presence of fluorine has a powerful

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[1] H. Offermann, *Zeit. angew. Chem.*, 3, 615, 1890; F. Stolba, *Journ. prakt. Chem.*, (1), 89, 129, 1863; *Zeit. anal. Chem.*, 2, 396, 1863; J. Zellner, *Monats.*, 18, 749, 1897; T. Haga and Y. Osaka, *Chem. News*, 71, 98, 1895; S. L. Penfield, *ib.*, 39, 179, 1879; *Amer. Chem. Journ.*, 1, 27, 1879; H. Gilbert, *Corresp. Ver. anal. Chem.*, 3, 114, 1880; A. E. Haswell, *Rep. Anal. Chem.*, 6, 223, 1886; G. B. van Kampen, *Chem. Weekblad*, 8, 856, 1911; A. Hileman, *Amer. Journ. Sci.*, (4), 22, 329, 1906; N. Sahlbom and F. W. Hinrichsen, *Ber.*, 39, 2609, 1906; L. Schucht and W. Möller, *ib.*, 39, 3693, 1906; W. H. Adolph, *Journ. Amer. Chem. Soc.*, 37, 2500, 1915; C. R. Wagner and W. H. Ross, *Ind. Eng. Chem.*, 9, 1116, 1917; G. A. Shuey, *Journ. Assoc. Official Agr. Chem.*, 11, 147, 1928; D. S. Reynolds, W. H. Ross and K. D. Jacob, *ib.*, 11, 225, 1928; E. Bayle and L. Amy, *Compt. rend.*, 188, 792, 1929; V. Y. Anosov and S. K. Chirkov, *Journ. Applied Chem. (U.S.S.R.)*, 5, 1097, 1932; A. A. Borkovskii and N. A. Porfir'ev, *ib.*, 6, 984, 1933; O. Kallauner and K. Kuráš, *Stavivo*, 65, 1933; E. N. Isakov, *Zavodskaya Lab.*, 3, 896, 1934; S. N. Rozanov, *ib.*, 3, 791, 1934; *Zeit. anal. Chem.*, 102, 328, 1935; S. Bein (*Rep. Anal. Chem.*, 6, 169, 1886) collects and weighs the precipitated silica.

[2] G. Steiger, *Journ. Amer. Chem. Soc.*, 30, 219, 1908; W. H. Adolph, *ib.*, 37, 2500, 1915; H. E. Merwin, *Amer. J. Science*, (4), 28, 119, 1909; L. Fresenius, K. Schröder and M. Frommes, *Zeit. anal. Chem.*, 73, 65, 1928; O. Hackl, *ib.*, 97, 254, 1934; G. A. Shuey, *Journ. Assoc. Official Agr. Chem.*, 11, 147, 1928; H. J. Wichmann and D. Dahle, *ib.*, 16, 612, 619, 1933; G. R. Sharpless and E. V. McCollum, *Journ. Nutrition*, 6, 163, 1933; L. Szegö and B. Cassoni, *Giorn. Chim. Ind. Appl.*, 15, 599, 1933; E. Peyrot, *Ann. Chim. appl.*, 24, 74, 1934; I. M.

bleaching effect upon the yellow colour produced when a solution of a titanium salt is peroxidised by hydrogen peroxide. In this process a known volume of the solution containing the fluorine is mixed with a known amount of peroxidised titanium. The tint of this solution is compared in a colorimeter with that of a second solution containing an equivalent amount of titanium and the bleaching effect is recorded. The extent of the bleaching enables the amount of fluorine to be computed as indicated below.

Preparation of the Solution.—Fuse 2 grms. of the powdered and dry sample —say Cornish stone—with 8 grms. of sodium carbonate and extract the cold mass with hot water. Add 4 grms. of ammonium carbonate. Warm the mixture for a few minutes and continue the heating on a water bath until the ammonium carbonate is destroyed [1] and the volume of the liquid is small. Filter and wash; the filtrate and washings should not exceed 75 c.c.

Standard Solution.—Pipette 10 c.c. of the standard solution of titanium sulphate [2] into a 100 c.c. flask; add 4 c.c. of hydrogen peroxide and 3 c.c. of concentrated sulphuric acid. Make the solution up to the mark with water. 100 c.c. of this solution contain 0·01 grm. of TiO_2.

Test Solution.—Add 4 c.c. of hydrogen peroxide to the 75 c.c. of filtrate obtained from the 2 grms. of the sample under investigation. Then add 10 c.c. of the standard titanium solution.[3] Add about 4 c.c. of concentrated sulphuric acid to neutralise the sodium carbonate in the solution.[4] When the solution is neutral, it acquires a light orange tint. Add an aqueous solution of sodium carbonate, drop by drop, to neutralise the acid and discharge the colour. Then add a drop or two of sulphuric acid to restore the colour; add enough concentrated sulphuric acid [5] to make a 3–5 per cent. solution. Make the solution up to 100 c.c. The solution contains 0·01 grm. of TiO_2.

The Comparison.—These two solutions should have the same tint, because they have the same amount of titanium per c.c.; but if the test solution contains fluorine, it will have a paler tint owing to the bleaching effect of this element. The comparison can be made in Nessler's glasses—6 cm. long, 2·7 cm. diameter, placed over a white surface in diffused daylight. The comparison can also be made in a suitable colorimeter—say Duboscq's colorimeter. The depths of the liquids in the two tubes are adjusted so that when

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Korenman, *Zeit. anorg. allgem. Chem.*, **216**, 33, 1933; W. Dawihl, *Keram. Rundschau*, **42**, 607, 1934; R. C. Warren, C. T. Gimingham and H. J. Page, *Journ. Agr. Sci.*, **15**, 516, 1925; L. A. Steinkoenig, *Ind. Eng. Chem.*, **11**, 463, 1919. The intense reddish-brown colour furnished by titanic salts with dihydroxymaleic acid is also bleached by fluorine in an analogous way— H. J. H. Fenton, *Journ. Chem. Soc.*, **93**, 1064, 1908. A. Gautier and P. Clausmann (*Compt. rend.*, **154**, 1670, 1753, 1912) separate the fluorine as lead fluoride, and the lead is subsequently determined colorimetrically (page 350). For the nephelometric determination of fluorine, see R. E. Stevens, *Ind. Eng. Chem. Anal. Ed.*, 8, 248, 1936.

[1] To prevent the formation of ammonium sulphate later on. Ammonium sulphate leads to high results, because it, like fluorine, bleaches the titanium solution.

[2] STANDARD TITANIUM SULPHATE.—Heat an intimate mixture of 1 grm. of titanium dioxide and 3 grms. of ammonium persulphate until the vigorous reaction has ceased. Drive off the ammonium persulphate by heat. Heat the residue with 20 c.c. of concentrated sulphuric acid (sp. gr. 1·84) until the acid fumes copiously. Pour the cold solution into 800 c.c. of water. The titanium oxide soon dissolves. Then add 37·5 c.c. of concentrated sulphuric acid and make the solution up to a litre. The solution contains 0·001 grm. of TiO_2 and about 0·1 grm. of H_2SO_4 per c.c. Verify the result by a determination of the TiO_2 by the method given in footnote 5, page 191.

[3] The hydrogen peroxide prevents the precipitation of $Ti(OH)_4$ by the alkali carbonates.

[4] I. P. Alimarin (*Zavodskaya Lab.*, **5**, 1440, 1936) neutralises the excess of sodium carbonate with dilute sulphuric acid, using *p*-nitrophenol as indicator. This avoids losses by spurting.

[5] That is, about 3 c.c. of the concentrated sulphuric acid per 100 c.c. of solution.

the tubes are changed right to left, and left to right, the tints appear the same, or the left one appears uniformly darker.[1] The ratio

$$\frac{\text{Depth of standard solution}}{\text{Depth of test solution}} \times 100$$

is then noted. This number is taken as an abscissa, and the corresponding ordinate of the standard curve, fig. 157, gives the amount of fluorine in the two-gram sample. For instance, if the test solution had a depth 4·41 cm. and the standard solution 3·75 cm., the ratio is

$$\frac{3·75}{4·41} \times 100 = 85·0$$

The ordinate corresponding with the abscissa 85 is 0·0006. This latter number represents the amount of fluorine in the given sample. Supposing that 2 grms. of the sample be undergoing analysis, the sample would be reported to contain 0·03 per cent. of fluorine.

The Standard Bleaching Curve.—A standard solution of sodium fluoride is prepared from pure, recrystallised, washed and strongly ignited sodium fluoride
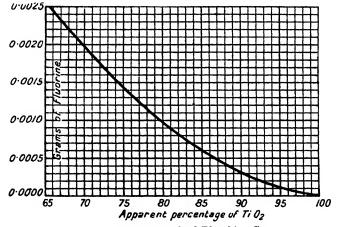
FIG. 157.—Steiger's Standard Bleaching Curve.

by dissolving 2·2104 grms. of sodium fluoride in a litre of water. 1 c.c. of this solution is equivalent to 0·001 grm. of fluorine. A series of comparisons is made with standard fluoride solutions, each containing 4 c.c. of hydrogen peroxide and 3 c.c. of concentrated sulphuric acid, against similar solutions containing no fluoride. In this way a curve similar to that shown in fig. 157 is obtained. The following results were observed:—

Fluorine	.	.	0·0005	0·0010	0·0015	0·0020	0·0025 grm.
Titania	.	.	86·41	79·24	74·67	69·60	65·40

The numbers in the last line represent the apparent amounts of titanium measured in terms of the ratio

$$\frac{\text{Depth of liquid free from fluorine}}{\text{Depth of liquid containing fluorine}} \times 100$$

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[1] Since the left eye is usually more sensitive to the tint.

Errors.—The method is not satisfactory when the amount of fluorine exceeds 0·125 per cent., that is, 0·0025 grm. on a two-gram sample. If more fluorine be present, the amount of the sample taken must be lessened. If the temperature deviates appreciably from the temperature prevailing at the time the standard bleaching curve was made, the tint of the solution will appear paler and high results will be obtained. Sodium and potassium sulphates in large amounts have a bleaching effect, but, if a large excess of sulphuric acid be present, the effect is not so marked. Aluminium sulphate intensifies the colour and thus gives low results. Quantities of silica less than 0·1 grm. have but little influence on the result. The method of preparing the sample for comparison eliminates most of the silica and alumina and what remains has practically no influence on the result. Phosphoric acid bleaches the solution like fluorine, but the amount usually present in silicates does no harm. The tints are dependent on the proportion of sulphuric acid in the solution, and it is very important to adjust the solutions undergoing comparison so that they contain approximately the same proportion of sulphuric acid, both in making up the solutions for the standard bleaching curve, and in making the tests. According to Blum,[1] when but "little acid is present, the colours cannot be properly matched. This is the case, for instance, with 0·003 grm. fluorine in 2 per cent. sulphuric acid solutions; but with 10 per cent. of sulphuric acid a fairly satisfactory comparison was possible with as much as 0·005 grm. of fluorine." Wichmann and Dahle[2] find that (1) the bleaching action of the fluorine increases with increasing acidity to a maximum corresponding with a hydrogen ion concentration of about 1·5 and then rapidly decreases until it becomes practically zero at $p_H = 2·5$; (2) the bleaching per unit of fluorine increases as the concentration of fluorine increases and the concentration of titanium decreases; (3) the bleaching is proportional to the quantity of fluorine present up to a certain limit, above which the bleaching per unit of fluorine decreases. They recommend that the determination should be carried out at a controlled p_H of $1·50 \pm 0·02$ and say that, in these circumstances, as little as 0·002 mgrm. of fluorine can be determined. Korenman[3] makes the comparison by diluting the stronger solution with water until it matches the weaker, whereas Hackl[4] adds to the standard solution a standard solution of sodium fluoride until a match in colour is obtained. As a result of his investigation, Merwin states that an "accuracy of 0·0002 grm. may be expected. The probable error is therefore not half as great as with standard gravimetric methods."

II. De Boer's Process.

The bleaching effect of fluorine on the lake formed between zirconium and alizarinsulphonic acid was first used by de Boer and Basart[5] for the determination of fluorine. The method has been modified and employed in recent years for the colorimetric determination of fluorine,[6] particularly in natural waters. The procedure recommended by Smith and Dutcher is as

[1] W. Blum in *Bull. U.S. Geol. Sur.*, **700**, 228, 1919.
[2] H. J. Wichmann and D. Dahle, *Journ. Assoc. Official Agr. Chem.*, **16**, 612, 619, 1933; **19**, 313, 320, 1936.
[3] I. M. Korenman, *Zeit. anorg. allgem. Chem.*, **216**, 33, 1933.
[4] O. Hackl, *Zeit. anal. Chem.*, **97**, 254, 1934.
[5] J. H. de Boer and J. Basart, *Zeit. anorg. Chem.*, **126**, 213, 1926.
[6] J. and R. Casares, *Anal. Fis. Quim.*, **28**, 910, 1159, 1930; T. G. Thompson and H. J. Taylor, *Ind. Eng. Chem. Anal. Ed.*, **5**, 87, 1933; O. M. Smith and H. A. Dutcher, *ib.*, **6**, 61, 1934; I. M. Kolthoff and M. E. Stansby, *ib.*, **6**, 118, 1934; J. M. Sanchis, *ib.*, **6**, 134, 1934; S. E. Harris and W. G. Christiansen, *Journ. Amer. Pharm. Assoc.*, **25**, 306, 1936.

follows:—The neutral solution of the fluoride, free from sulphates,[1] is acidified with 3 c.c. of hydrochloric acid (1 : 1) and 5 c.c. of zirconium-quinalizarin reagent [2] are added. The solution is diluted to a definite volume, say 100 c.c., and thoroughly shaken. After 20 minutes the colour is compared with that of a series of standards made from a solution of sodium fluoride containing 0·01 grm. of fluorine per litre. It is important that the test and standard solutions should contain exactly the same amounts of acid and of zirconium-alizarin reagent and that they should be compared at equal times after preparation.[3]

§ 350. The Determination of Fluorine as Gaseous Silicon Fluoride—Oettel and Hempel's Process.

The simplest method for the determination of fluorine in silicates decomposable by sulphuric acid, and exact enough for commercial requirements, is to treat the substance with concentrated sulphuric acid, and to measure the volume of the gaseous silicon fluoride evolved during the reaction. Oettel, and Hempel and Scheffler,[4] have devised special instruments—called fluorometers—for this purpose. Oettel's fluorometer is illustrated in fig. 158.

Charging the Apparatus.—It consists of a decomposition flask A, a burette B and a levelling tube C. The flask has a volume of about 100 c.c.; its neck is widened into a cup, which is closed by a ground glass stopper. The side arm of the flask ends in a ground glass joint which fits into the cup on the upper end of the burette. This burette is made from a barometer tube of a total volume of 100–150 c.c. and is graduated in fifths of a c.c. Immediately below the cup on the burette is a mark and lower down is the zero graduation, the volume enclosed between the two marks being 7–10 c.c. The burette is filled with dry mercury, which is brought to zero by means of the levelling tube C. The thick-walled rubber tube connecting the levelling tube with the burette is then clamped, so that the level of the mercury cannot alter. The levelling tube C is then lowered somewhat and clamped; finally the burette is filled with concentrated sulphuric acid [5] up to the mark below the cup. Transfer to the decomposition flask, which must be perfectly dry, 0·3 to 0·5

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[1] If the solution is obtained as in Steiger's process, it must be exactly neutralised with hydrochloric acid. Sulphates, if present, are precipitated by the addition of a slight excess of 2 per cent. barium chloride solution and filtering.

[2] ZIRCONIUM-QUINALIZARIN REAGENT.—Equal parts of a 0·14 per cent. solution of quinalizarin (1 : 2 : 5 : 8-tetrahydroxyanthraquinone) in 0·30 per cent. sodium hydroxide solution and a 0·87 per cent. solution of zirconium nitrate are mixed and the mixture is diluted to 1 in 40.

[3] For other colorimetric methods for determining fluorine, see M. D. Foster, *Journ. Amer. Chem. Soc.*, **54**, 4464, 1932; *Ind. Eng. Chem. Anal. Ed.*, **5**, 234, 238, 1933; W. D. Armstrong, *ib.*, **5**, 300, 1933; H. V. Smith, *ib.*, **7**, 23, 1935; T. G. Thompson and H. J. Taylor, *ib.*, **5**, 87, 1933. A. Mayrhoffer, A. Wasitzky and W. Korn (*Mikrochem.*, **20**, 29, 1936) distil off the fluorine as in Carnot's process (page 731), absorb the silicon tetrafluoride in sodium hydroxide and then determine the silica in solution colorimetrically by the molybdate method, page 686.

[4] F. Oettel, *Zeit. anal. Chem.*, **25**, 505, 1886; W. Hempel and W. Scheffler, *Zeit. anorg. Chem.*, **20**, 1, 1899; W. E. Burk, *Journ. Amer. Chem. Soc.*, **23**, 824, 1901; J. Shuch, *Zeit. Landw. Vers. West. Oest.*, **9**, 531, 1904; O. R. Böhm, *Oester. Chem. Ztg.*, **10**, 61, 1907; A. Jodlbauer, *Zeit. Biol.*, **44**, 259, 1903; H. Wislicenus, *Zeit. angew. Chem.*, **14**, 706, 1901; F. G. Hawley, *Ind. Eng. Chem.*, **18**, 573, 1926.

[5] "The concentrated sulphuric acid used in the work is made by heating the concentrated acid of the laboratory in a porcelain dish with flowers of sulphur. The acid is then poured off from the molten sulphur and evaporated down to two-thirds its volume." W. Hempel, *Methods of Gas Analysis*, London, 322, 1892.

grm. of finely powdered cryolite (or fluorspar), intimately mixed with twenty times its weight of calcined quartz.[1]

Evolution of the Gas.—Connect the decomposition flask to the burette and let the whole apparatus stand 15 minutes to assume the temperature of the room. Add 50 c.c. of concentrated sulphuric acid to the flask by means of a pipette.[2] Insert the stopper and pour mercury into the cups on the flask and burette so as to seal the joints. The 100 c.c. bulb *A* will now be about half full. Open the clamp to connect the burette with the levelling tube. The pressure of the air is reduced by the fall of the mercury. Read the thermometer and barometer. Heat the flask by means of a small flame until the sulphuric acid begins to boil. (As the silicon fluoride is evolved, the mercury sinks and the column of sulphuric acid above it covers the walls of the burette, thus removing any traces of moisture.) This should take about 20 minutes. In another 5 to 10 minutes the reaction will be complete. Adjust the levelling tube so as to keep the level of mercury some 10 to 15 cm. lower than the level in the burette. Shake the flask from time to time as much as possible by moving the whole stand, but without jerking the mercury from the mercury-sealed joints. Let the flask cool for about 2 hours, when it should have attained the temperature of the room. Raise the levelling tube from time to time during the cooling to counterbalance the diminished pressure of the cooling gas. Level the mercury in the burette and levelling tube. Read the burette, thermometer and barometer, and also the height of the column of sulphuric acid above the mercury. Normally, neither the pressure nor the temperature changes during an experiment, but if they do the appropriate correction must be made for the change in volume of the air in flask *A*. Since this correction amounts only to a few tenths of a c.c., the volume of the air in the dead space of the flask need only be known approximately. Suppose the following results have been obtained:—

Fig. 158.—Oettel's Fluorometer.

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[1] "The silicon dioxide required is best obtained by pulverising rock crystal and igniting the powder in a combustion tube in a current of oxygen." W. Hempel, *l.c.*; see also page 732. P. Drawe (*Zeit. angew. Chem.*, **25**, 1371, 1912) uses 0·5–0·6 grm. of felspar (instead of quartz) along with 5 grms. of anhydrous copper sulphate (page 625) to make sure that the moisture is removed.

[2] Do not touch the flask needlessly, or it may be warmed and cause an expansion of the gas.

Readings and Calculations.—Weight of cryolite, 0·5261 grm. Temperature, t_0, at the beginning, 17°; barometer at the beginning, 757·4 mm.; temperature, t_1, at the end, 18°; barometer at the end, 757·4; height of column of sulphuric acid, 40 mm., which is equivalent to 5·4 mm. mercury. Volume of dead space in flask, 80 c.c. Volume of gas collected 85·9 c.c. Since the temperature has risen 1° during the experiment, the air in the flask will have expanded by $80 \times \frac{1}{273} = 0·3$ c.c. approximately. Hence the corrected volume of the gas is $85·9 - 0·3 = 85·6$ c.c. This volume is measured at 18° C. and a pressure of $757·4 - 5·4 = 752$ mm., and the volume at 0° and 760 mm. will be $(85·6 \times 273 \times 752)/(291 \times 760) = 79·5$ c.c. Concentrated sulphuric acid absorbs silicon tetrafluoride and experiments show that with the quantities of acid used here an average correction of $+ 1·4$ c.c. must be made; hence $79·5 + 1·4 = 80·9$ c.c. of SiF_4 were produced during the reaction. But 1 c.c. of silicon fluoride at 0° and 760 mm. pressure represents 0·0033886 grm. of fluorine. Hence, 80·9 c.c. represent 0·2741 grm. of fluorine per 0·5261 grm. of cryolite; or the cryolite has 52·1 per cent. of fluorine.

In illustration of the accuracy of the process, Oettel quotes the following results with calcium fluoride:

| Found | . | . | 0·2183 | 0·2349 | 0·1051 | 0·2792 | 0·2776 | grm. |
| Calculated | . | . | 0·2173 | 0·2350 | 0·1050 | 0·2801 | 0·2782 | grm. |

This is all that can be desired in commercial work. To get accurate results, it is highly important to exclude all traces of moisture from the generating apparatus.[1]

§ 351. Volumetric Processes for the Determination of Fluorine.

A number of methods have been proposed for the volumetric determination of fluorine, a necessary and obvious preliminary to all of which is to obtain the fluorine wholly in solution. Guyot's process, resuscitated by Greeff,[2] is based on the reactions—

$$3NaF + FeCl_3 = 3NaCl + FeF_3$$

and

$$3NaF + FeF_3 = Na_3FeF_6$$

The sodium ferric fluoride thus formed is only sparingly soluble in water and gives no coloration with potassium thiocyanate. Hence the fluoride solution, containing an excess of potassium thiocyanate, is titrated with a standard solution of ferric chloride until a permanent red colour is obtained under specified conditions. Fairchild modifies the method by adding an excess of the ferric chloride solution and determining the excess iodometrically.[3]

In Boer and Basart's process,[4] the fluoride solution and a blank are treated with a solution of zirconium oxychloride and sodium alizarin sulphonate. The blank solution is then titrated with a standard solution of potassium

[1] P. Drawe (*Zeit. angew. Chem.*, **25**, 1371, 1912).

[2] P. Guyot, *Compt. rend.*, **71**, 274, 1870; **73**, 273, 1871; A. Greeff, *Ber.*, **46**, 2511, 1913; I. Bellucci, *Ann. Chim. appl.*, **1**, 441, 1914; B. Visintin, *ib.*, **24**, 315, 1934; M. Giordani, *ib.*, **24**, 496, 1934; N. K. Smitt, *Chem. Trade Journ.*, **71**, 325, 1922; *Bull. Bur. Biotech.*, **176**, 1922; L. D. Hammond, *Ind. Eng. Chem.*, **16**, 938, 1924; W. D. Treadwell and A. Köhl, *Helv. Chim. Acta*, **8**, 500, 1925.

[3] J. G. Fairchild, *Journ. Wash. Acad. Sci.*, **20**, 141, 1930; H. V. Churchill, *Ind. Eng. Chem.*, **23**, 996, 1931; C. S. Boruff and G. B. Abbott, *ib.*, *Anal. Ed.*, **5**, 236, 1933; M. D. Foster, *ib.*, **5**, 238, 1933; H. V. and M. C. Smith, *Arizona Expt. Station Tech. Bull.*, **43**, 213, 1932; H. Hale, *Oklahoma Agr. and Mech. Eng. Expt. Station Bull.*, **3**, 35, 1932.

[4] J. H. de Boer and J. Basart, *Zeit. anorg. allgem. Chem.*, **126**, 213, 1926.

fluoride until the degree of fading produced in it matches the colour of the test solution.

In yet other methods,[1] the neutral fluoride solution is titrated with a standard solution of aluminium chloride, cerous, yttrium, zirconium or thorium nitrate, until the precipitation of the fluoride is complete—various indicators or a potentiometer may be used to determine the end-point. With cerous nitrate, a measured excess can be added and the excess determined by titration with potassium permanganate at 70°–80° in the presence of zinc oxide.

Willard and Winter give the following details for the titration with thorium nitrate.[2] An aliquot portion of the fluoride solution, which must contain no interfering elements or acid radicals, is diluted to, say, 20 c.c. and a few drops[3] of the indicator solution[4] are added. If necessary, dilute hydrochloric acid is added to discharge any colour. An equal volume of ethyl alcohol is added and the mixture titrated over a white surface with standard thorium nitrate solution[5] until the colour of the zirconium-alizarin lake just reappears. With 0·01N-thorium nitrate solution, a correction must be made for the fluorine which combines with the indicator. This is determined by titrating an equal number of drops of the indicator with a 0·01N-fluoride solution. The indicator blank increases with the age of the indicator solution and is higher than the blank in the actual fluoride titration. The method is said to be accurate for titrating pure and dilute fluoride solutions, but it is not accurate in the presence of large amounts of thorium fluoride. Some prefer to obtain the fluorine equivalent of the thorium nitrate titration from a graph prepared empirically.

§ 352. The Analysis of Calcium Fluoride—Fluorspar.

The process of § 350 may be used for all silicates which are completely decomposed by sulphuric acid, as indicated on page 739. Hence, calcium fluoride is easily treated by the process. In commercial analyses of fluorspar, calcium fluoride, silica and calcium carbonate are usually determined. In special cases the amount of lead, iron, zinc, sulphur and barium sulphate may be needed.[6] One rapid process is as follows:—

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[1] W. D. Treadwell and A. Köhl, *Helv. Chim. Acta*, **9**, 470, 1926; A. Kurtenacker and W. Jurenka, *Zeit. anal. Chem.*, **82**, 210, 1930; G. Batchelder and V. W. Meloche, *Journ. Amer. Chem. Soc.*, **53**, 2131, 1931; **54**, 1319, 1932; N. Allen and N. H. Furman, *ib.*, **55**, 90, 1933; D. M. Hubbard and A. L. Henne, *ib.*, **56**, 1078, 1934; F. J. Frere, *Ind. Eng. Chem. Anal. Ed.*, **5**, 17, 1933; **6**, 124, 1934; I. V. Tananaev and G. S. Savchenko, *Journ. Applied Chem.* (*U.S.S.R.*), **7**, 229, 1934; N. Y. Ugnyachev and E. A. Bilenko, *Ukrain. Khem. Zhur.*, **12**, 34, 1937.

[2] H. H. Willard and O. B. Winter, *Ind. Eng. Chem. Anal. Ed.*, **5**, 7, 1933; E. W. Scott and A. L. Henne, *ib.*, **7**, 299, 1935; W. M. Hoskins and C. A. Ferris, *ib.*, **8**, 6, 1936; W. D. Armstrong, *ib.*, **8**, 384, 1936; C. S. Boruff and G. B. Abbott, *ib.*, **5**, 236, 1933; H. V. Churchill, R. W. Bridges and R. J. Rowley, *ib.*, **9**, 222, 1937; O. B. Winter and L. Butler, *Journ. Assoc. Official Agr. Chem.*, **16**, 105, 1933; G. A. Shuey, *ib.*, **17**, 149, 1934; D. S. Reynolds, *ib.*, **17**, 323, 1934; **18**, 108, 1935; D. Dahle and H. J. Wichmann, *ib.*, **20**, 297, 1937; W. D. Armstrong, *Journ. Amer. Chem. Soc.*, **55**, 1741, 1933.

[3] Three drops are needed for 20 c.c. of solution, increasing to 6 drops for 50–75 c.c.

[4] INDICATOR SOLUTION.—Dissolve (1) 1 grm. of zirconium nitrate, $Zr(NO_3)_4.5H_2O$, in 250 c.c. of water, (2) 1 grm. of sodium alizarin sulphonate in 100 c.c. of ethyl alcohol. Filter off the residue from (2) and add 150 c.c. of ethyl alcohol to the filtrate. Mix three parts of solution (1) with two parts of solution (2) as and when needed.

[5] Standardise the thorium nitrate solution against a 0·02N-solution of pure lithium or sodium fluoride.

[6] For barium and sulphur determinations in fluorspar by fusion in a bomb with Parr's fusion mixture (pages 707 to 708), see H. G. Martin, *Journ. Ind. Eng. Chem.*, **1**, 462, 1909. For the analysis of soluble fluorides, see J. G. Dinwiddie, *Amer. Journ. Sci.*, (4), **42**

1. *Calcium Carbonate.*—Heat 2 grms. of the dried (110°) material to constant weight. The loss in weight represents carbon dioxide. This amount of carbon dioxide, multiplied by 2·2746, represents the calcium carbonate.[1] This procedure assumes that both organic matter and combined moisture are absent. The carbon dioxide can best be determined gravimetrically (see pages 624 and 625).

Lundell and Hoffman [2] recommend the following method for the determination of silica and calcium fluoride:—

2. *Silica.*—Digest 1 grm. of the sample on a water bath for 10 minutes with 3 c.c. of a mixture of 20 c.c. of bromine and 80 c.c. of glacial acetic acid. Add 10 c.c. of water and 10 c.c. of a 20 per cent. solution of potassium bromide which has been saturated with bromine. Digest for 40 minutes. Then add 5 c.c. of 50 per cent. ammonium acetate solution and digest for a further 10 minutes. Add paper pulp, filter and wash with hot water. Dry, ignite at a dull red heat and weigh the residue. Determine the silica in it by the loss in weight after a double evaporation with about 3 c.c. of hydrofluoric acid. It is recommended that the ignitions should be made at or about 650°.

3. *Calcium Fluoride.*—Digest half a gram of the sample, preferably in a platinum crucible, on a water bath for 30 minutes with 15 c.c. of 10 per cent. acetic acid to remove any calcium carbonate and sulphate. Filter and wash well with hot water. Dry and ignite the residue at a dull red heat in the crucible. Cool, add to the residue about 3 c.c. of hydrofluoric acid and 2 c.c. of sulphuric acid and evaporate to dryness; rinse down the walls of the crucible with about another cubic centimetre of sulphuric acid and again evaporate to dryness. This treatment eliminates any silica and converts the calcium fluoride into sulphate. Immerse the crucible in 150 c.c. of warm 5 per cent. hydrochloric acid and, when its contents have dissolved, thoroughly rinse out the crucible. Boil for 10 minutes and, if any insoluble residue remains, filter it off, wash and ignite in the crucible.[3] The filtrate is treated with hydrogen sulphide, then made ammoniacal and finally saturated with hydrogen sulphide. Any iron, aluminium or zinc present in the sample will be precipitated here as sulphide. After allowing the precipitate to settle, filter and wash the residue with a one per cent. solution of ammonium chloride, containing a little ammonium sulphide. Acidify the filtrate and washings

464, 1916; A. Travers, *Compt. rend.*, **173**, 836, 1921; H. Flisik, *Ind. Eng. Chem.*, **17**, 307, 1925; E. C. Roper and E. B. R. Prideaux, *Journ. Soc. Chem. Ind.*, **45**, 109T, 1926; A. V. Frost, *Trans. Inst. Pure Chem. Reagents (Moscow)*, **10**, 53, 1931; I. Tananaev and G. S. Savchenko, *Journ. Applied Chem. (U.S.S.R.)*, **7**, 1071, 1934. For the analysis of cryolite, see F. Cherpillod, *Ann. Fals.*, **30**, 232, 1937.

[1] W. J. Waring, *Chem. Eng.*, **4**, 23, 1906; *ib.*, **3**, 65, 1905; L. Westerburg, *Chem. Ztg.*, **26**, 967, 1902; A. W. Gregory, *Chem. News*, **92**, 184, 1905.
Calcium carbonate is sometimes determined by digesting, say, 1 gram of the finely powdered sample with 10 c.c. of a 10 per cent. solution of acetic acid for about an hour on a water bath. The residue is filtered off through an ashless filter-paper, washed about four times with water, and the filter-paper "ashed" at as low a temperature as possible. The loss in weight would represent the amount of calcium carbonate in the given sample were it not for the fact that calcium fluoride is slightly soluble in acetic acid. E. Bidtel (*Journ. Ind. Eng. Chem.*, **4**, 201, 1912; **6**, 265, 1914) says that, in using this method with clean crystals of fluorspar, 0·0015 grm. is dissolved per gram of sample. See also E. Oliver, *Rev. universelle Mines*, **14**, 25, 1922. Lundell and Hoffman (*l.c.*) find the solubility of calcium fluoride in dilute acetic acid decreases as the percentage of calcium carbonate in the sample of fluorspar increases.

[2] G. E. F. Lundell and J. I. Hoffman, *U.S. Bur. Standards Journ. Research*, **2**, 671, 1929.

[3] The residue may contain sulphates of lead and barium and also undecomposed calcium fluoride. To recover the latter, evaporate the residue to dryness with a few c.c. of hydrofluoric and sulphuric acids. Digest with 1 to 2 c.c. of hydrochloric acid, filter and wash. The filtrate is added to the main solution.

with a slight excess of hydrochloric acid and boil until all the hydrogen sulphide has been expelled. Oxidise any sulphur or sulphides present to sulphates by adding a 20 per cent. solution of potassium bromide, saturated with bromine, until the solution has a permanent yellow tinge. Boil until all the bromine has been expelled. It is now assumed that the above treatment has removed any calcium not present as fluoride and all associated impurities in the fluorspar. The calcium in the final solution is precipitated as oxalate and weighed as oxide, following the standard procedure (page 202); a double precipitation is unnecessary. The weight of calcium oxide multiplied by 1·3923 gives the corresponding amount of calcium fluoride. A correction of +0·20 per cent. should be made to compensate for the solubility of calcium fluoride in dilute acetic acid. This process [1] is believed to give results accurate to ±0·25 per cent.

§ 353. The Analysis of Sodium Silicofluoride.

The fluorine cannot be determined as silicon fluoride, because, on treatment with acids, the silicon fluoride is accompanied by hydrogen fluoride, which etches glass. Thus, with concentrated sulphuric acid,

$$Na_2SiF_6 + H_2SO_4 = Na_2SO_4 + SiF_4 + 2HF$$

Hence, on heating a known weight of the substance with concentrated sulphuric acid in a platinum dish, until the white fumes of sulphuric acid are given off, sodium sulphate and sulphates of the other bases present will remain.[2] The bases can be determined in the usual way. Sodium silicofluoride can be titrated with 1·0N-sodium hydroxide, using phenolphthalein as indicator. The reaction is represented:

$$Na_2SiF_6 + 4NaOH = 6NaF + SiO_2 + 2H_2O$$

Commercial samples contain about 95 per cent. of sodium silicofluoride.

The loss on ignition of sodium silicofluoride does not represent the "water" because, on heating, this salt decomposes into sodium fluoride and silicon fluoride: $Na_2SiF_6 = 2NaF + SiF_4$. To determine the water, use the method given on page 642, namely, fusion in glass tubes with lead oxide.[3]

Hydrofluosilicic acid is a by-product in the manufacture of artificial manures. The acid is treated with soda or common salt in order to precipitate sodium silicofluoride. Hence the commercial salt may be contaminated with chlorides, which can be determined as described below.

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[1] For the analysis of fluorspar, see F. Wöhler, *Pogg. Ann.*, **48**, 87, 1839; R. Fresenius, *Anleitung zur quantitativen chemischen Analyse*, Braunschweig, **1**, 435, 1875; K. Daniel, *Zeit. anorg. Chem.*, **38**, 257, 1904; G. R. Doyle, *Chem. News*, **118**, 304, 1919; C. E. Gifford, *Ind. Eng. Chem.*, **15**, 526, 1923; W. W. Scott, *ib.*, **16**, 703, 1924; P. Drawe, *Chem. Ztg.*, **49**, 497, 1925; K. Brauer and Ruthsatz, *ib.*, **51**, 618, 1927; E. Bailleux, *Ingénieur Chimiste*, **9**, 230, 1925; *Bull. Soc. chim. Belg.*, **35**, 305, 1926; F. Sautier, *Chim. et Ind.*, Special No., 202, 1926; A. Lebrun, *Rev. Belg. ind. Verrières*, **2**, 220, 1931; I. Tananaev, *Journ. Applied Chem. (U.S.S.R.)*, **5**, 445, 1932; A. K. Kudrevalov, *Compt. rend. Acad. Sci. (U.S.S.R.)*, **4**, 42, 1934.

[2] For the direct determination of silica and fluorine, use the process indicated on page 637 For the transformation into chlorides, use hydrochloric acid (1 acid, 2 water by volume)— F. Stolba, *Chem. Centr.*, (3), **11**, 595, 1880. Evaporation with perchloric acid quantitatively converts water-soluble and insoluble fluorides into perchlorates—G. A. Shuey, *Journ. Assoc. Official Agr. Chem.*, **17**, 149, 1934.

[3] H. Rose, *Ausführliches Handbuch der analytischen Chemie*, Braunschweig, **2**, 667, 1851; P. Jannasch, *Praktischer Leitfaden der Gewichtsanalyse*, Leipzig, 357, 1904; E. Hintz and H. Weber, *Zeit. anal. Chem.*, **30**, 30, 1891.

§ 354. The Properties of Silver Chloride.

Chlorides are determined by adding a solution of silver nitrate to an acidified solution of the chloride. The white curdy[1] precipitate of silver chloride is washed, dried and weighed. In 1859, Mulder[2] pointed out that the solubility of silver chloride in the mother liquid is sufficient to disturb all quantitative analyses based upon the precipitation of silver chloride, and Cooke[3] considered that about 0·0001 grm. of silver chloride is dissolved per 100 c.c. of liquid used in washing. It is now considered to be a well-established fact that freshly precipitated silver chloride is soluble in water to the extent of about 0·000156 grm. per 100 c.c. at 18°, and 0·00218 grm. at 100°.[4] The solubility of freshly precipitated silver chloride steadily diminishes to about a milligram per litre when the precipitate is left standing in contact with the mother liquid. This change in the solubility is generally supposed to be due to the fact that the solubility of many salts, which are only slightly soluble in water, is affected by the size of the grain. The smaller the grain, the greater the solubility.[5] Silver chloride when first precipitated is in a very finely divided condition and the small grains grow into larger grains at the expense of the very smallest granules on long standing. The solution is also generally warmed to coagulate any colloidal silver chloride which may be formed, and so prevent a turbid filtrate passing through the filter-paper.

The presence of a small excess of either silver nitrate or sodium chloride reduces the solubility of the precipitated chloride.[6] A large excess of hydrochloric acid, alkali chlorides or nitrates, other metallic chlorides or silver nitrate increases the solubility of silver chloride. Thus, the solubility of silver chloride in different strengths of hydrochloric acid at 21° is, according to Whitby, as follows:

| Hydrochloric acid | 0 | 1 | 5 | 10 | per cent. |
| Silver chloride | 0·00156 | 0·0002 | 0·0033 | 0·0555 | grm. per litre. |

[1] If but small quantities of silver chloride be present, the solution only becomes turbid. The suspended particles then settle very slowly. See C. H. Greene and L. D. Frizzell, *Journ. Amer. Chem. Soc.*, 58, 516, 1936.

[2] G. J. Mulder, *Die Silberprobiermethoden*, Leipzig, 311, 1859; *Chem. News*, 4, 99, 125, 137, 204, 231, 1861; 5, 2, 1862.

[3] J. P. Cooke, *Amer. J. Science*, (3), 21, 220, 1881; *Chem. News*, 44, 234, 1881; D. Lindo, *ib.*, 45, 193, 1882.

[4] C. H. Pfaff, *Handbuch der analytischen Chemie*, Altona, 2, 283, 1821; G. J. Mulder, *Die Silberprobiermethoden*, Leipzig, 1859; J. L. Gay-Lussac, *Ann. Chim. Phys.*, (2), 58, 218, 1835; A. Ditte, *ib.*, (5), 22, 551, 1881; J. S. Stas, *ib.*, (5), 3, 177, 1874; *Compt. rend.*, 73, 998, 1871; C. St Pierre, *ib.*, 73, 1090, 1871; F. Kohlrausch and F. Rose, *Wied. Ann.*, 50, 127, 1893; *Zeit. phys. Chem.*, 12, 242, 1893; F. Kohlrausch, *ib.*, 50, 355, 1905; 64, 129, 1908; C. Hoitsema, *ib.*, 20, 272, 1896; W. Böttger, *ib.*, 46, 602, 1903; 56, 83, 1906; H. M. Goodwin, *ib.*, 13, 645, 1894; A. F. Hollemann, *ib.*, 12, 132, 1893; A. A. Noyes and D. A. Kohr, *ib.*, 42, 336, 1902; R. Abegg and A. J. Cox, *ib.*, 46, 1, 1903; *Zeit. Elektrochem.*, 9, 892, 1903; A. Thiel, *Zeit. anorg. Chem.*, 24, 57, 1900; G. S. Whitby, *ib.*, 67, 107, 1910; R. Lorenz and E. Bergheimer, *ib.*, 137, 141, 1924; J. P. Cooke, *Amer. Journ. Science*, (3), 21, 220, 1881; *Chem. News*, 44, 234, 1881; F. Field, *ib.*, 3, 17, 1861; A. C. Melcher, *Journ. Amer. Chem. Soc.*, 32, 54, 1910; A. Thiel, *ib.*, 37, 508, 1915; A. F. Hill, *ib.*, 30, 68, 1908; W. G. Eversole and R. W. McLachlan, *ib.*, 54, 864, 1932; E. W. Neuman, *ib.*, 54, 2195, 1932; C. van Rossem, *Chem. Weekb.*, 9, 203, 396, 1912; L. Rolla, *Atti Accad. Lincei*, (5), 22, ii, 104, 1913; Z. Głowczyński, *Koll. Chem. Beihefte*, 6, 147, 1914; S. Popov and E. W. Neuman, *Journ. Phys. Chem.*, 34, 1853, 1930.

[5] W. H. Wollaston, *Phil. Trans.*, 103, 51, 1813; W. Ostwald, *Zeit. phys. Chem.*, 34, 495, 1900; G. Hulett, *ib.*, 37, 385, 1901; 47, 357, 1904; S. E. Sheppard and R. H. Lambert, *Coll. Symp. Mon.*, 6, 265, 1928; *Brit. Chem. Abs.*, B, 976, 1929.

[6] C. Hoitsema, *Zeit. phys. Chem.*, 20, 272, 1896.

The lower solubility of silver iodide and bromide has led to the use of soluble iodides and bromides in place of chlorides for precipitating silver from solutions (page 342). The solubilities of the three halides in grams per litre in water at 20° are:

AgCl	AgBr	AgI
0·00156	0·000084	0·0000028

The silver chloride during precipitation is inclined to carry down, or "occlude" or "adsorb," silver nitrate [1] and sodium chloride. These substances are associated in some way with the precipitated chloride so that the impurities are not removed by washing. In general, the longer the precipitate remains in contact with the mother liquid, the greater the difficulty in removing the adsorbed salts. Precipitates formed in dilute solutions are generally more amenable to washing than precipitates formed in concentrated solutions.

White silver chloride dries (in the dark) to a white pulverulent mass which becomes yellow when heated. Silver chloride fuses at about 455° to a transparent yellow liquid which attacks platinum very rapidly. At a high temperature, silver chloride begins to volatilise. When the molten mass is cooled, it forms a colourless or pale yellow mass. Silver chloride is easily reduced to the metal when heated in contact with organic matter,[2] and hence a difficulty arises if a filter-paper is used in separating the precipitate from the mother liquid.

§ 355. The Gravimetric Determination of Chlorides.

The silicate is fused with sodium carbonate,[3] as described for the determination of sulphur (page 701). The clear aqueous extract of the fused mass, or an aliquot portion of it, is acidified with nitric acid in the cold.[4] Heat the solution to about 60°. Gradually add, with constant stirring,[5] about 5 c.c. of an aqueous solution of silver nitrate.[6] When the precipitate has settled, add a few more drops of the silver nitrate solution and, if a precipitate be formed, more silver nitrate must be added. When the addition of silver nitrate no longer produces a precipitate, heat the mixture to 60° [7] and let the mixture settle in the dark,[8] say, overnight. Decant the cold solution through a

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[1] J. S. Stas, *Œuvres complètes*, Bruxelles, **1**, 337, 1894.

[2] E. Murmann (*Oester. Chem. Zeit.*, (2), **19**, 115, 1916; *Chem. Zentr.*, (2), 427, 1916) adds ash-free paper pulp before or after precipitation of the chloride and on subsequent ignition spongy, metallic silver remains.

[3] All the reagents should be tested for possible and probable contamination with chlorides.

[4] H. S. Washington (*Manual of the Chemical Analysis of Rocks*, New York, 160, 1904) prefers to decompose the silicate with a mixture of nitric and hydrofluoric acids (free from chlorides) in a platinum basin; boil for an hour; filter through a platinum or rubber funnel into a platinum basin; and precipitate the silver chloride in the presence of an excess of nitric acid. For the solubility of silver chloride in nitric acid, see Z. Główczyński, *Koll. Chem. Beihefte*, **6**, 147, 1914; A. F. Scott and C. R. Johnson, *Journ. Amer. Chem. Soc.*, **52**, 3586, 1930; C. R. Johnson and G. W. Low, jun., *ib.*, **55**, 2262, 1933.

[5] So as to reduce as much as possible the adsorption of salts by the precipitate.

[6] SILVER NITRATE SOLUTION.—Dissolve 3·4 grms. of silver nitrate in 100 c.c. of water (0·2E).

[7] E. Alefeld (*Zeit. anal. Chem.*, **48**, 79, 1909) adds 5 c.c. of ether to the solution before adding silver nitrate, in order to coagulate the precipitate. A Gooch crucible (packed with asbestos) is used for the filtration. It is moistened with ether before the suction is applied. The filtration may here be done immediately after the precipitation. The precipitate is washed with water. M. Whittel (*Chem. Ztg.*, **7**, 559, 1883) recommends a drop of chloroform to coagulate the precipitate.

[8] White silver chloride soon becomes violet and finally dark brown, almost black, when exposed to the light. Some claim that there is then an appreciable loss, possibly owing to the formation of a sub-chloride. G. J. Mulder, *Die Silberprobiermethoden*, Leipzig, 59, 1859. See also J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, London, **3**, 408, 1923.

(7·5 cm.) filter-paper.[1] Wash by decantation a few times with water just acidified with nitric acid. Transfer the precipitate to the filter-paper[2] and wash with the acidulated water until a drop of the washings gives no turbidity with hydrochloric acid. Dry the precipitate between 90° and 95° and separate it from the paper. Keep the precipitate in a covered watch-glass. Incinerate the paper in a small weighed porcelain crucible—not platinum. Do not allow the paper to burn with a flame. When the carbon has disappeared, the chloride will be reduced to metal. Add a few drops of nitric acid and warm the crucible to dissolve the metallic silver; add a few drops of hydrochloric acid; evaporate the solution to dryness; then transfer the precipitate in the watch-glass to the crucible. Heat the crucible and contents gently, but not sufficiently high to fuse the silver chloride (455°). Cool and weigh as silver chloride. If the silver chloride so obtained is quite soluble in ammonia, the work is finished; if an insoluble residue remains, proceed as follows:—

Purification of the Silver Chloride Precipitate.—In order to purify the precipitate from silica, alumina, or other impurities, if present, dissolve the precipitate in the crucible in aqueous ammonia; filter the solution to separate the insoluble residue; wash the residue with ammonia; acidify the solution with nitric acid; add a drop of silver nitrate; filter and wash the precipitated silver chloride as before. This precipitate can be collected on filter-paper, but a Gooch crucible with ignited asbestos is preferable. See page 467.

Calculations.—The weight of the silver chloride multiplied by 0·24737 represents the corresponding amount of chlorine. The sum of the different constituents in a silicate analysis may exceed the limit 100 ± 0.5 if appreciable amounts of chlorine be present, because some of the chlorine will have been reckoned as oxygen in evaluating the bases. By the same process of reasoning as was used for fluorine, every n per cent. of chlorine obtained must be multiplied by 0·2256 in order to get the equivalent amount of oxygen, and the product is appended to the analysis in this form: "Less x per cent. of oxygen, equivalent to n per cent. of chlorine."

Jannasch's Filter Tube.—Instead of a Gooch crucible, the stoppered tube as recommended by Jannasch[3] may be used—fig. 159. This is fitted with a

FIG. 159.—Jannasch's Filter and Weighing Tube.

layer of glass-wool, from 0·5 to 1·0 cm. thick, in the neck, B; above this is a layer, C, of asbestos such as is used for the Gooch crucible, 0·5 to 1·0 cm. thick. The narrow end of the tube is fitted into the filtration flask by means of a one-hole rubber stopper. Water is run through the tube until any particles of loose glass-wool have all been washed into the flask. Dry the tube for two or three hours at 150° and when cooled (50°–60°) insert the stopper

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[1] If the silver chloride contains no impurities, it is preferably filtered through a Gooch crucible with ignited asbestos.

[2] If any traces of chloride stick tenaciously to the beaker, dissolve them in ammonia, transfer the solution to a weighed crucible, acidify with nitric acid, evaporate to dryness, dry at 150° and weigh. Add the weight to that of the main mass of silver chloride.

[3] P. Jannasch, *Praktischer Leitfaden der Gewichtsanalyse*, Leipzig, 11, 1904. Neither Jannasch's tube nor the Gooch crucible is used for collecting the first precipitate if the silver chloride is to be freed from silica.

A and cool in a desiccator. Insert the stopper *D* and weigh. Filter the silver chloride precipitate through the tube and dry at 180°–200°, as indicated above. Insert the stoppers as before and weigh. The increase in weight represents the silver chloride.

The Determination of Soluble Chlorides in Clays.—The chlorine present in the soluble salts in clays can be determined gravimetrically as just described; or volumetrically,[1] as indicated on pages 65 and 68; or by the turbidity method. The turbidity method is conducted in a similar manner to the turbidity process (page 718) for the determination of sulphates.[2] A solution of silver nitrate must be substituted for barium chloride; and sodium chloride substituted for calcium sulphate.

§ 356. The Determination of Silver.

The determination of silver is a reciprocal process to the determination of chlorides. In the latter case a silver salt is added to the soluble chloride; and in the former case a soluble chloride is added to the solution containing silver.[3] In each determination the precipitated silver chloride is prepared for weighing in the same way. The weight of the silver chloride multiplied by 0·75263 gives the corresponding amount of silver.

Benedickt and Gans' Gravimetric Process.[4]—Add a slight excess of potassium iodide to the solution containing an excess of about 10 c.c. dilute nitric acid.[5] Any silver present is precipitated as silver iodide. If too great an excess of potassium iodide be added, some silver iodide may remain in solution. The solution is then heated. If any lead be present, the precipitated lead iodide will be decomposed by this treatment, soluble lead nitrate will be formed and iodine will be set free. The latter is volatilised. When the solution is free from the colour of iodine, the silver iodide is filtered off, washed and weighed as in the case of silver chloride. The weight of silver iodide multiplied by 0·4594 gives the corresponding amount of silver. Hampe considers this "the most accurate of the wet processes for the determination of silver." It can be used for determining the amount of silver in lead compounds.

For the volumetric processes for silver, *vide* pages 65 and 68; for the cupellation process, page 336; and for metallic precipitation with cadmium or zinc,[6] follow the method of page 313.

Whitby's Colorimetric Process.[7]—This process is based on the development

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[1] F. Muck (*Zeit. anal. Chem.*, **22**, 222, 1883), in the presence of organic matter, evaporated the liquid to dryness and moistened the residue with a solution of potassium or sodium hydroxide free from chlorine. Then warm the mass with chlorine-free potassium permanganate solution until the colour of the solution remains green. A drop of alcohol will destroy the green colour. Filter and wash. The chlorine is determined in the filtrate as usual.

[2] T. W. Richards, *Internat. Cong. App. Chem.*, **8**, i, 423, 1913; P. A. Guye, *Journ. Chim. phys.*, **10**, 145, 1913; F. Meyer and A. Stahler, *Zeit. anorg. Chem.*, **77**, 255, 1913.

[3] It appears to be advantageous to precipitate the silver by the addition of a soluble bromide, since silver bromide is less soluble than silver chloride; and still more advantageous to precipitate the silver as silver iodide, since this salt is even less soluble than silver bromide.

[4] R. Benedickt and L. Gans, *Chem. Ztg.*, **16**, 4, 12, 44, 1892; W. Hampe, *ib.*, **18**, 1899, 1894; F. Pisani, *Compt. rend.*, **43**, 1118, 1856; F. Field, *Chem. News*, **3**, 17, 1861.

[5] If antimony be present, the addition of tartaric acid prevents its contaminating the precipitated silver iodide.

[6] A. W. Clasen, *Journ. prakt. Chem.*, (1), **97**, 217, 1866. For reduction with hydroxylamine, see A. Lainer, *Monats.*, **9**, 533, 1888; with aluminium, N. Tarugi, *Gazz. Chim. Ital.*, **33**, ii, 223, 1904; with cobalt, C. Goldschmidt, *Zeit. anal. Chem.*, **45**, 87, 1906.

[7] G. S. Whitby, *Internat. Congress App. Chem.*, **7**, 12, 1910; *Zeit. anorg. Chem.*, **67**, 62, 1910. See page 336. For the colorimetric determination of silver as colloidal sulphide, see K. C. D. Hickman, *Phot. Journ.*, **62**, 512, 1922; S. E. Sheppard and A. Ballard, *Journ. Franklin Inst.*, **206**, 659, 1928.

of a brown or yellow colour when a solution of a silver salt is heated with a little sodium hydroxide and an organic substance (e.g. dextrine, gum arabic, cellulose—filter-paper—starch, cane-sugar). The intensity of the coloration is proportional to the amount of silver present. The colour is sensitive enough to show the presence of silver in 50 c.c. of a solution containing one part of silver in 25,000,000 parts of solution; and it is possible to estimate 0·000002 grm. of silver in 50 c.c. of solution, i.e. 0·00004 grm. of silver per litre.[1]

Standard Solution.—Pipette 5 c.c. of a standard silver solution [2] into a 150 c.c. beaker. Dilute the solution to 50 c.c. Add a few drops of a concentrated solution of cane-sugar. Immerse the beaker in a bath of boiling water for 2 minutes; add 5 drops of a 1·0N-solution of sodium hydroxide and heat the mixture for 20–30 seconds after the colour has appeared.[3] Cool the solution and transfer it to a Nessler's glass.

Test Solution.—The silver solution under investigation is appropriately diluted and treated as described for the standard solution.[4] 50 c.c. of the solution are transferred to a Nessler's glass. The tint of this solution should be of nearly the same intensity as the tint of the standard solution. If not, either the standard or the test solution must be diluted and the operations (development of colour) repeated.

The Comparison.—Water is run from a burette into the Nessler's glass containing the standard solution, until the colour is of the same intensity in both glasses. The number of c.c. of water needed to dilute the 50 c.c. of the standard solution to the same intensity of colour as that of the 50 c.c. of the test solution gives the necessary data for calculating the amount of silver in the test solution (page 192)

Whitby says that ammonia should be absent, but minute traces of copper, zinc, mercury, bismuth, cadmium and lead, in quantities insufficient to give an appreciable precipitate with sodium hydroxide, do not interfere with the result.

Jelley's Colorimetric Process.—Jelley [5] says that Whitby's process also fails in the presence of cyanides and thiosulphates and, moreover, that the colour is due partly to the colloidal silver and partly to the coloured products from the decomposition of the sugar or other carbohydrate used in the reduction. Jelley finds that very dilute ammoniacal solutions of silver are reduced by sodium hyposulphite, $Na_2S_2O_4$, giving clear yellow colloidal solutions, in which the depth of colour varies linearly with the silver content between 2 and 16 mgrms. per litre. Gelatin is added as a protective colloid to keep the silver in a highly dispersed form.

Standard Solution.—Pipette 9·27 c.c. of 0·1N-silver nitrate (or weigh out 0·1575 grm. of pure silver nitrate) into a litre flask, add 25 c.c. of ammonia solution (sp. gr. 0·88) and dilute to the mark with copper-free distilled water. 1 c.c. of this standard contains 0·1 mgrm. of silver.

Test Solution.—An aliquot portion, say from 10–40 c.c., of the ammoniacal silver solution is pipetted into a 50 c.c. graduated flask. Add 10 c.c. of

[1] F. Jackson, *Journ. Amer. Chem. Soc.*, **25**, 992, 1903; W. Böttger, *Zeit. angew. Chem.*, **25**, 1992, 1912.

[2] SILVER NITRATE SOLUTION.—The standard silver nitrate solution should contain the equivalent of about 0·00001 grm. of silver per c.c. The standard solution should be prepared the same day as the determination is made; otherwise its tint deepens if it be allowed to stand for any length of time.

[3] Do not heat more than about 2 minutes.

[4] If no coloration appears after the solution has been heated 2 minutes, it can be assumed that silver is absent.

[5] E. E. Jelley, *Journ. Soc. Chem. Ind.*, **51**, 191T, 1932.

ammoniacal gelatin solution[1] and about 0·04 grm. of dry sodium hypo-sulphite. Dilute to the mark with approximately 1·0N-ammonia and shake well. Pour the whole of the solution into a dry boiling tube and warm to 50° in a water bath until the colour develops.

From previous experience, an amount of the standard solution is taken which will give an approximate match in colour when treated similarly and the colours of the two solutions are then compared in a colorimeter. Copper, cadmium, cobalt and nickel interfere. If these are present, an aliquot portion of the solution is treated with bromine water and hydrobromic acid and evaporated until the silver bromide has coagulated. The precipitate, which may also contain lead and thallium bromides, is filtered off through a sintered glass filter crucible and washed with water. The crucible is placed in a small beaker and the precipitate digested in the cold for 3–4 hours with 10 c.c. of concentrated ammonia. After filtering and washing, the filtrate is diluted so that it contains about 10 mgrms. of silver per litre.

§ 357. The Determination of Iodine.

Iodine, to the extent of 0·01–0·2 per cent., is not uncommonly present in mineral phosphates. It can be detected by digesting the finely powdered phosphate with concentrated sulphuric acid in a flask so arranged that a cur-rent of air is aspirated first through the flask, then through carbon disulphide or chloroform. The pink or violet colour of the solution shows the presence of iodine. Iodine is of no known technical importance in the silicate industries. Hence, the subject can be dismissed very briefly.

Thiercelin[2] determines iodine in phosphates, etc., by digesting a large quantity of the substance, say 100 grms., with a mixture of equal parts of sulphuric acid and water in a 500 c.c. flask or retort arranged so as to conduct the vapours into potash lye contained in suitable absorption tubes, say, fig. 147. The mixture in the flask is boiled (about 30 minutes) until all the vapours of iodine have been driven into the absorption tubes. The alkaline solution from the absorption tubes is treated with an excess of sulphurous acid to convert the iodates into iodides: $KIO_3 + 3SO_2 + 3H_2O = KI + 3H_2SO_4$.

The iodine absorbed by the lye can be determined as silver iodide by adding an excess of silver nitrate to the solution neutralised with nitric acid, and then adding an excess of nitric acid, in which silver iodide is almost insoluble.[3] The precipitated silver iodide is treated as if it were silver chloride (page 746); but silver iodide is not so readily reduced as the chloride and it may even be safely ignited with the filter-paper. The weight of silver iodide multiplied by 0·5406 gives the corresponding amount of iodine.

Sometimes iodine is determined as cuprous iodide[4] by adding a solution

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[1] AMMONIACAL GELATIN SOLUTION.—Digest 2 grms. of pure, ash-free gelatin in a little water until softened, then warm until it dissolves; add 100 c.c. of ammonia (sp. gr. 0·88) and dilute to 1000 c.c. with copper-free distilled water. Warm the solution on a water bath for 6–7 hours at 95°.

[2] M. Thiercelin, *Bull. Soc. chim.*, (2), **22**, 435, 1874.

[3] If the solution be first acidified with nitric acid, there is a risk of liberating iodine. If the solution be coloured with iodine, it is best to add a little sulphurous acid to decolorise it :—$SO_2 + I_2 + 2H_2O = 2HI + H_2SO_4$.

[4] F. Mohr, *Zeit. anal. Chem.*, **12**, 366, 1873; H. Zenger, *Archiv Pharm.*, (3), **3**, 137, 1873; J. Krutwig, *Ber.*, **17**, 341, 1884; E. Fleischer, *A System of Volumetric Analysis*, London, 97, 1877.

of ammonium cuprous chloride [1] to the solution of the iodide acidified with hydrochloric acid, and containing a sufficient excess of ammonium chloride to prevent the precipitation of cuprous chloride by the aqueous solution. The precipitated cuprous iodide is collected on a tared filter-paper, or better in a Gooch crucible, dried and weighed as Cu_2I_2. This method, however, offers no particular advantage over the silver iodide process.

[1] Copper turnings are digested in a solution of cupric chloride and ammonium chloride, acidified with hydrochloric acid. Sufficient ammonium chloride must be present to prevent the reagent giving a precipitate when diluted with water.

CHAPTER XLIV.

THE RATIONAL ANALYSIS OF CLAYS.[1]

§ 358. Clays.

IT may be desirable to preface this chapter with a few explanatory words. *Kaolin* is a general word applied to *china clay rock* and to *china clay* obtained by the washing of china clay rock. The term *clay* not only covers all the different varieties of clay but also a substance approximating to $Al_2O_3.2SiO_2.2H_2O$ in composition. This formula is supposed to represent a constituent common to all clays, and which has hence been variously termed "clay base," "clay substance," "clay proper," "clay matter," "ideal clay." The word *kaolinite* is applied to a crystalline mineral with the empirical formula $Al_2O_3.2SiO_2.2H_2O$. We are almost sure that a colloidal substance with the same empirical composition exists in most, probably in all, clays. This is here called *clayite* for distinction, since it has several properties different from kaolinite. If it were not for the dread of multiplying terms, a word would be coined to include both clayite and kaolinite. We use the term *argillaceous matter* for that heterogeneous mixture which is removed from a clay by the treatment used in the method of "rational analysis." It includes clayite, kaolinite and other minerals.[2]

Clays are produced by the weathering and disintegration of various kinds of rocks which occur on or near the surface of the earth. If the clay occurs where it has been formed, it is called a *primary or residual clay*; and if the clay has been carried elsewhere it is called a *secondary or transported clay*. The transported clays are the washings and sweepings of the hills, which Nature has accumulated as her rubbish-heaps in convenient places. Kaolinite or clayite and quartz are common to nearly all clays, while felspar and mica are so common in clays that these four constituents can reasonably be regarded as the *primary constituents* of clays. The list of *secondary constituents*, which usually occur in relatively small quantities, is very extensive. In the first place, we find fragments of various kinds of rock—*e.g.* granite, trachyte, rhyolite, syenite; and in the second place, fragments of numerous minerals have been reported in clays [3] :—

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[1] Much of the original matter in this chapter is the result of experiments made on the *rationale* of the method of rational analysis during the investigation of the composition of dusts for Sir Henry Cunynghame, chairman of the *Committee appointed to Inquire into the Causes and Remedies for Coal Dust Explosions in Coal Mines*. The reader must thank the chairman for permission to use such experiments as we thought fit for this chapter. Most of the work was done by Messrs A. D. Holdcroft and C. Edwards, during 1911.

[2] J. W. Mellor, *Trans. Cer. Soc.*, 8, 23, 1909; *Pot. Gaz.*, 34, 927, 1909.

[3] See H. G. Schurecht, *Journ. Amer. Cer. Soc.*, 5, 3, 1922; J. S. McDowell, *ib.*, 9, 55, 1926.

Anatase, andalusite, apatite, augite, bronzite, calcite, chlorite, corundum, cyanite, diaspore, dolomite, dumortierite, enstatite, epidote, fluorspar, garnet, gilbertite, glaucophane, gypsum, hæmatite, hornblende, hydrated alumino-silicates related to clayite, hypersthene, ilmenite, leucoxone, lignite, limonite, magnesite, magnetite, nepheline, nontronite, olivene, prehnite, pyrites, rutile, scapolite, selenite, serpentine, siderite, sillimanite, spinel, staurolite, titanite (sphene), topaz, tourmaline, vivianite, zeolite, zircon, zoisite.

The secondary constituents are usually present in small quantities and in a more or less advanced state of decomposition. The *rational analysis* is an attempt to express the composition of a clay in terms of the primary constituent minerals.

§ 359. The Separation of Minerals by Treatment with Chemical Reagents.

Clay is a heterogeneous mixture of several different minerals. The chemical methods for estimating the minerals in clays are based on differences in the rates at which the various minerals are attacked by different reagents. The separation of the constituents of a clay which are soluble in water (page 716) is a comparatively simple example, whereas the digestion of clay with hydrofluoric acid is more complicated. Quartz, felspar, leucite and minerals rich in silica are in general quickly decomposed by treatment with hydrofluoric acid under conditions where sillimanite, staurolite, topaz, tourmaline, zircon and many titanium minerals are but little attacked; while mica, hornblende and sphene are partially decomposed.[1] Unfortunately, the differences in the rates of attack of the more important minerals in clays by known reagents are not usually great enough to allow a perfect separation. Before one mineral is completely decomposed, others will have succumbed to the attack. Hence, the products of decomposition of the one mineral will be more or less contaminated with products derived from the partial decomposition of other minerals. Hydrochloric acid, for example, is frequently used to remove iron oxides, and calcium, magnesium and iron carbonates from clays. But if the clay contains olivine, serpentine, chlorite, nepheline, epidote, leucite and zeolites, the acid may do too much work, for these minerals are more or less decomposed by the same treatment. Similar remarks apply, *mutatis mutandis*, to the action of sulphuric acid. Compare with page 591.

The analysis of clays by digesting the powdered sample in sulphuric acid, followed by solutions of caustic alkalies, was common enough at the end of the eighteenth and at the beginning of the nineteenth centuries, as is evidenced by the analyses of Bergmann, Hochmeimer, Kirwan, Klaproth, Lampadius, Schönbauer, Vauquelin and Westrumb.[2] In 1835, Forchhammer[3] showed

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[1] F. Fouqué, *Compt. rend.*, 75, 1090, 1872; 79, 869, 1874; F. Fouqué and M. Levy, *Minéralogie micrographique*, Paris, 116, 1879; J. B. Mackintosh, *School Mines Quart.*, 7, 384, 1886; *Journ. Amer. Chem. Soc.*, 8, 210, 1886; *Chem. News*, 54, 102, 1886. Mackintosh believes that, the denser the mineral, the less is it attacked by the acid; and that the rate of attack by hydrofluoric acid does not depend upon the proportion of silica, but rather on the nature of the bases. K. Obbeke, *Neues Jahrb. Min.*, 1, 455, 1881; J. Hazard, *Zeit. anal. Chem.*, 23, 158, 1884; *Chem. News*, 50, 33, 1884.

[2] T. Bergmann, *Opuscula Physica et Chemica*, Holmiæ, 2, 399, 1780; C. F. A. Hochmeimer, *Mineralogische Chemie*, Leipzig, 1792; R. Kirwan, *Physich-chemische Schriften*, Berlin, 1783; M. H. Klaproth, *Beiträge zur chemischen Kenntniss der Mineralkörper*, Berlin, 1795; W. A. Lampadius, *Handbuch zur chemischen Analyse der Mineralkörper*, Freiburg, 1801; J. A. Schönbauer, *Neue analytische Methode die Mineralien und ihre Bestandtheile Richtig zu Bestimmen*, Wien, 1805; L. N. Vauquelin, "Anleitung zur chemischen Analyse der Fossilen," *Scherer's Journ.*, 3, 410, 1799; J. F. Westrumb, *Kleine physisch-chemische Abhandlungen*, Leipzig, 1785.

[3] G. Forchhammer, *Pogg. Ann.*, 35, 331, 1835; *Ann. Mines*, (3), 7, 517, 1835.

that, when certain clays are digested with sulphuric acid, the ultimate composition of the soluble portion corresponds very nearly with the formula $Al_2O_3.2SiO_2.2H_2O$; while the residual insoluble portion is mainly felspar and quartz. Hence, Forchhammer attempted to determine the mineralogical composition of certain clays by successive treatment with different reagents. After leaching out the constituents soluble in hydrochloric acid, he extracted the residue alternately with hot sulphuric acid and an aqueous solution of sodium carbonate. This treatment was supposed to remove the argillaceous matter. We shall, however, soon see that a variety of other minerals, *e.g.* mica, felspar, fluorspar, are more or less attacked by this treatment. Forchhammer's process has been more or less modified by Brongniart and Malaguti, Seger,[1] among others, and extensively used—principally in Germany—with Brongniart's designation, *l'analyse rationelle.* The so-called rational analysis is a first approximation or attempt to represent the mineralogical composition of a clay in terms of the three important minerals—kaolinite, felspar and quartz—and hence it can also be called a "mineralogical analysis," *vide* page 590. The essential features of the process are:—

Remove the argillaceous matter by digestion with hot concentrated sulphuric acid and wash the residue alternately with alkaline lye and hydrochloric acid.[2] The difference between the weight of the dried residue and the original sample represents argillaceous matter. The residual felspathic and quartz detritus is evaporated to dryness with hydrofluoric and sulphuric acids and the alumina determined in the residue. The amount of felspar corresponding to the alumina, thus found, is computed and the quartz is determined by difference. One *modus operandi* is as follows:—

§ 360. The Rational or Mineralogical Analysis of Clays.

Preliminary Treatment.—If the clay contains soluble salts, they are removed by the process given on page 716; if it contains colloidal silica, this can be removed as given on page 765; and if it contains carbonates—calcium, magnesium, iron—or free iron oxide, these should be removed by digesting, say, 5 grms. with dilute hydrochloric acid (page 591) before treatment with sulphuric acid. The hydrochloric acid also removes colloidal aluminium and iron hydroxides, and it attacks some of the argillaceous matters, as well as apatite, hæmatite (powdered), magnetite, leucite, sodalite, nepheline, olivine, wollastonite and most of the zeolites; while scapolite, plagioclase, serpentine, chlorite and the more compact iron oxides are but slowly attacked. Hence, Weinschenk[3] recommends chloric acid, in place of hydrochloric acid, to avoid breaking up silicates when the carbonates are decomposed. The washed

[1] A. Brongniart and J. Malaguti, *Arch. Mus. Hist. Nat.*, 2, 219, 1841; J. Aron, *Notizblatt*, 10, 226, 1874; M. Finkner, *ib.*, 3, 119, 1867; C. Bischof, *ib.*, 11, 120, 1875; H. A. Seger, *ib.*, 12, 245, 1876; *Tonind. Ztg.*, 1, 272, 1877; G. Lunge and C. Millberg, *Zeit. angew. Chem.*, 10, 393, 425, 1897; *Monit. Sci.*, 11, 867, 1897; J. Burian and J. Juránek, *Chem. Listy*, 1, 1912; *Silikat-Zeit.*, 2, 12, 1914; W. A. Selvig, *Carnegie Inst. Tech. Min. Met. Invest. Bull.*, 21, 1925; A. Shaw, *Analyst*, 59, 446, 1934; L. R. L. Dunn, *ib.*, 60, 35, 1935; O. Boudouard and J. Lefranc, *Bull. Soc. chim.*, (4), 31, 1145, 1922; A. Stassens, *15me Cong. Chim. Ind.* (*Bruxelles*, 1935), 155, 1936; O. Kallauner (with J. Simane), *Zprávy Ceskoslov. Keram. Spole.*, 11, 24, 1934; *Chem. Zentr.*, (2), 2865, 1934.

[2] In future, it will be convenient to refer to this sequence of operations as the "acid-alkali treatment."

[3] B. Weinschenk, *Die gesteinbildenden Mineralien*, Freiburg, 11, 1907; New York, 150, 1912. For the action of organic acids on minerals, see page 590.

residue is dried and weighed. The loss in weight represents the matters soluble in the acid. The carbon dioxide, if desired, can be determined by a gravimetric process, and the lime, magnesium and iron determined in the acid solution if necessary. If the carbon dioxide be determined by weight (page 625), the acid-alkali treatment can be applied to the washed residue, or to a new sample, as described below, and an allowance made when the clay substance is determined.

In illustration, Altofts' shale gave 4·42 per cent. of carbon (page 616) and 2·44 per cent. of carbon dioxide (page 625). The solution of the shale in hydrochloric acid contained much iron and very little lime or magnesia. Hence it was inferred that the shale contained ferrous carbonate. One part by weight of carbon dioxide corresponds with 2·632 of ferrous carbonate, and accordingly the shale contained the equivalent of $2·44 \times 2·632 = 6·42$ per cent. of ferrous carbonate.

Removal of Argillaceous Matters.—The residue from the preceding operation, or, if carbonate be absent, about 5 grms. of the clay, dried at 110°, is placed in a 1000 c.c. porcelain basin. Add 100 c.c. of water and triturate the mixture with a rubber-tipped glass rod or rubber pestle, so that the clay is thoroughly disintegrated.[1] This procedure breaks down clots of clay, if present, and so lessens the risk of any clay escaping the action of the acid. Add 100 c.c. of a mixture of equal volumes of concentrated sulphuric acid and water to the clay "slip." Cover the basin with a clock-glass. If the clay is dark-coloured, add a few drops of concentrated nitric acid to destroy the organic matter.[2] Warm the mixture over an Ostwald's heater,[3] with frequent stirring, until the water is all evaporated and the acid begins to fume vigorously. The temperature should be such that this occupies between 45 and 60 minutes. The dish is allowed to cool for about half an hour and then it is nearly filled with water[4] and the contents thoroughly mixed. Wash the rod and cover-glass. Let the dish stand undisturbed for about four hours to permit the residue to settle. Decant the liquid contents of the dish into a 2-litre beaker, taking care that no solid particles are transferred from the dish.[5] Add 300 c.c. of Lunge's

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[1] The addition of a drop or two of aqueous ammonia or soda lye greatly helps the disintegration of the mass, as does boiling the mixture for about 10 minutes, but any water lost by evaporation should be restored. The clay must not be powdered in an agate mortar for this operation, as is done in the ultimate analysis.

[2] If the clay contains organic matter, *e.g.* lignite, rootlets, A. Sabeck (*Chem. Ind.*, **25**, 90, 1902) recommends the addition of about 15 c.c. of nitric acid after the clay has been digesting with the sulphuric acid for a couple of hours. If chloric acid be used for decomposing the carbonates, much of the organic matter will be removed at the same time. H. Stremme (*Ker. Rund.*, **22**, 325, 1914; J. Burian and J. Juránek, *Chem. Listy*, **37**, 1, 1913; *Silikat-Zeit.*, **2**, 12, 1914) uses chromic acid. K. A. Vesterberg *et al.* (*Ark. Kemi Min. Geol.*, **9**, No. 14, 1, 1925; *Chem. Zentr.*, (2), 1553, 1925; H. Boege, *Chem. Erde*, **3**, 341, 1927; O. Kallauner and J. Matejka, *Sprechsaal*, **47**, 423, 1914; *Chem. Zentr.*, (2), 732, 1914) treat the clay with 20 per cent. hydrochloric acid, ignite the residue at *c.* 700° and again digest it with the acid. Compare G. Linck, *Chem. Erde*, **3**, 370, 1927. Note, organic matter is included with "argillaceous matter" by this method of treatment. The error, if neglected, is serious with some clays—*e.g.* black ball clays.

[3] W. Ostwald, *Zeit. anal. Chem.*, **31**, 180, 1892; F. Muck, *ib.*, **28**, 661, 1889; J. Volhard, *Liebig's Ann.*, 285, 330, 1895.

[4] Care is necessary in adding water to concentrated sulphuric acid. Some prefer to lift the cover of the dish a little and spurt water from the wash-bottle on the under side of the clock-glass.

[5] In pouring off the bulk of the liquid (down a glass rod in the usual way) the sediment is disturbed. It is best to decant all but about 100 c.c. of the liquid. Let this stand about 15 minutes to settle and again decant. This enables more liquid to be poured off with less risk of losing the insoluble residue.

solution [1] to the residue and heat the mixture, with frequent stirring, until it begins to boil. Wash the rod and cover-glass. Let the mixture cool for about a couple of hours. The liquid should be clear. If the sediment does not settle and flocculent masses remain in suspension,[2] it is probable that the clay is but imperfectly decomposed.[3] Decant off the alkaline lye, stir up the residue with about 500 c.c. of concentrated hydrochloric acid and boil the mixture for about five minutes; this dissolves the iron hydroxide, etc. Stir up with water. Let all stand for about five hours. Decant off the acid.[4] Repeat the treatment with about 150 c.c. of Lunge's solution, followed by digestion with 200 c.c. of hydrochloric acid. Stir the mass with about 200 c.c. of water, decant and wash the residue with dilute hydrochloric acid (1 volume of acid, 2 volumes of water) into a close-felted filter-paper; [5] wash twice with the dilute acid and three times with water. Ignite the filter-paper with its contents in a weighed platinum crucible. The ignited residue is generally styled "felspar and quartz" and treated as described below. The difference between the weight of clay subjected to the acid-alkali treatment and the weight of the "felspar and quartz" represents "argillaceous matter"— also called "clay substance." In illustration of the weighings, and method of calculation, the rational analysis of Altofts' shale [6] may be cited:

Clay originally taken	.	.	.	.	5·0000 grms.
Crucible and residue	.	.	.	.	35·3236 ,,
Crucible empty	.	.	.	.	33·2950 .,
Quartz and felspar.	.	.	.	2·0286 ,,
Soluble matter (difference [7])	.	.	2·9714 ,,

Hence, 59·43 per cent. of matter has been removed by the acid-alkali treatment and 40·57 per cent. remains as a residue. Preceding determinations (page 754) showed that this 59·43 per cent. of soluble matter contained:—

Carbonaceous matter	.	.	.	4·42 per cent.
Ferrous carbonate (siderite)	.	.	6·42 ,, ,,
Argillaceous matter (by difference)	.	48·59 ,, ,, .

[1] LUNGE'S SOLUTION.—Dissolve 100 grms. of crystallised sodium carbonate and 10 grms. of sodium hydroxide in water and make the solution up to a litre. Remember that this solution will dissolve silica from the glass of the bottle in which it is kept. A five or six per cent. solution of caustic soda is frequently used in place of Lunge's solution. Different workers also prescribe different strengths of caustic soda solution (see p. 761, footnote 1). Lunge's solution is fairly well known and there is at present no adequate reason for recommending a change.

[2] Flecks of silicic acid, organic matter and iron hydroxide will probably be present.

[3] J. A. Körner (*Beitrag zur Kenntniss der Elsässer Thone*, Strassburg, 1900) removes the soluble silica left after the action of the sulphuric acid as follows:—Wash the residue from the sulphuric acid treatment with dilute hydrochloric acid (1 : 3) and incinerate the residue to burn off the filter-paper. Digest the mass on a water bath for five minutes with 0·5 per cent. hydrofluoric acid; filter and wash with dilute hydrochloric acid; ignite and weigh as "quartz and felspar." Hydrofluoric acid of this strength is said not to attack the quartz appreciably.

[4] If flecks of clay be present, the sulphuric acid has not done its work. The residue is usually more or less gritty, although flecks of organic matter may be present.

[5] Note that in the filtration very fine particles of undecomposed felspar and quartz have a tendency to pass through the paper and thus swell the proportion of argillaceous matter, at the expense of the residue.

[6] We have purposely selected an awkward clay, because it enables us to emphasise the strength and weaknesses of the process of rational analysis.

[7] The filter-papers used were almost ashless.

Estimation of the Felspathic and Quartz Detritus.—The residue in the crucible is mixed with about 5 c.c. of water, about 4 drops of sulphuric acid and 15 c.c. of hydrofluoric acid.[1] The crucible is then placed on a sand bath or over a small flame and heated until its contents are nearly dry. Repeat the operation with the addition of more hydrofluoric acid. Let the mass cool, digest with water and add ammonium chloride and ammonia as indicated on page 164 for the precipitation of iron and aluminium hydroxides. Filter, wash with hot water, ignite and weigh. Call the mixture of oxides "alumina." Thus, with the above clay:

Crucible and contents	33·3477 grms.
Crucible empty	33·2986 ,,
"Alumina" precipitate	0·0491 grm.

Since one gram of alumina corresponds with 5·459 grms. of potash felspar, the weight of the precipitate, multiplied by 5·459, gives its equivalent in potash felspar.[2] We thus obtain $5·459 \times 0·0491 = 0·2680$ grm. of felspar per 5 grms. of clay—that is, 5·36 per cent. of felspar.[3] We then have :—

Felspar and quartz residue . . .	40·57 per cent.
Felspar calculated	5·36 ,,
Quartz *débris*	35·21 ,,

Neglecting the second decimal, the rational analysis thus reads:

Carbonaceous matter	4·4 per cent.
Ferrous carbonate (siderite) . . .	6·4 ,,
Argillaceous matter	48·6 ,,
Felspathic detritus	5·4 ,,
Quartz *débris*	35·2 ,,

Errors.—Apart from the difficulties which arise from our ignorance of the nature of the constituent minerals and the fact that the acid and alkaline solutions do more work than accords with the hypothesis on which the process is based, the chief errors of manipulation are: (1) Incomplete decomposition of the kaolinite or clayite. (2) Imperfect removal of the products of the decomposition. These two errors make the felspathic detritus too high and the argillaceous matter too low. (3) Loss of a portion of the felspathic and quartz detritus either during the decantation [4] or by passage through the pores

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[1] M. Lindhorst, *Tonind. Ztg.*, 2, 435, 1878; K. Daniel, *Zeit. anorg. Chem.*, 38, 257, 1904. H. Rose's method (*Pogg. Ann.*, 108, 20, 1859) for driving off the silica by thoroughly mixing the residue with ammonium fluoride in an agate mortar and moistening with sulphuric acid may be used. Let the mixture stand in a warm place for a few hours, heat until the silicon fluoride has been driven off and repeat the treatment if any of the mixture has escaped decomposition. Fusion with sodium carbonate (page 144), as first recommended by Seger, is not so convenient.

[2] Attempts to remove felspar from the first residue by digesting the mixture at 200° with alkali phosphates and with microcosmic salt have not been successful, because the finely divided quartz is seriously attacked at the same time as the felspar—A. Müller, *Journ. prakt. Chem.*, (1), 95, 43, 1865; (1), 98, 14, 1866; *Zeit. anal. Chem.*, 5, 431, 1866; E. Laufer, *ib.*, 17, 368, 1878; *Ber.*, 11, 60, 935, 1878; E. Wunderlich, *ib.*, 14, 368, 2811, 1881; J. Hirschwald, *Journ. prakt. Chem.*, (2), 41, 360, 1880; E. A. Wülfing, *Neues Jahrb. Min. B.B.*, 7, 174, 1891; K. Haushofer, *Sitzber. Acad. Wiss. München*, 8, 1889.

[3] Some consider that a more exact determination of felspar can be obtained by determining the alkalies and not the alumina by the method of page 219.

[4] To avoid this error, some prefer to filter the decanted liquid and wash the residue with the acid and alkaline lye. E. Greiner, *Sprech.*, 42, 399, 413, 1909.

of the filter-paper. This error makes the argillaceous matter too high and the felspathic detritus too low.

The whole process occupies about two days. If a start be made in the morning, the first alkali and hydrochloric acid decantations can generally be done the first day. Of course, other work can be done while the sediments are settling. Thus, two analyses can be conducted side by side in two days. In order to get comparable or consistent results, it is highly important to follow the directions, *e.g.* concentration of reagents, time of heating, somewhat closely. The reason for this will now be discussed.

§ 361. The Effect of the Acid-Alkali Treatment on some of the Minerals in Clays.

Sulphuric acid decomposes the hydrated alumino-silicates and zeolites forming aluminium sulphate and silicic acid. The soda treatment removes the latter, hydrochloric acid the former. At the same time, the soda attacks [1] the felspar somewhat rapidly, while the accessory minerals hornblende, augite and biotite are attacked rather more slowly. Andalusite, epidote, prehnite and muscovite are but slightly attacked by the same reagent. It is therefore interesting to get some idea of the effect of the treatment with sulphuric acid, caustic soda and hydrochloric acid on the minerals usually found in clays. The samples were treated exactly as if they were being analysed by the "rational" process just described.

1. *Felspar.*—The felspar in clays is attacked by the acid-alkali treatment and finely divided felspar more vigorously than the coarse-grained mineral. In illustration, clear [2] crystals of albite (soda felspar) from Maderanerthal (Switzerland), and clear crystals of orthoclase (potash felspar) from Aletschgletscher (Switzerland), were powdered and treated as if they were samples undergoing "rational analysis" by the method described above. The results were:

	Coarse.	Fine.
Average diameter of grain .	0·082	0·032 mm.
Albite dissolved . . .	1·76	14·69 per cent.
Orthoclase dissolved . .	0·86	13·01 ,,

The term "coarse" here refers to powder which passed through a 120's lawn and remained on a 200's lawn, while "fine" refers to that which passed through the 200's lawn.[3] In further illustration of the effect of size of grain another series of determinations with a clear glassy sanidine from Wehr (Eifel) gave:

Average diameter of grain .	0·165	0·082	0·032 mm.
Sanidine dissolved . . .	0·34	0·64	15·64 per cent.

These results are plotted in fig. 160, which brings out the fact that, although the effect of the treatment on coarse-grained felspar is negligible, the effect on the small grains is vigorous. Sabeck says that if the clay contains no more

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[1] J. Lemberg, *Zeit. deut. geol. Ges.*, 35, 560, 1883; G. S. Tilley and J. D. Sullivan, *Journ. Amer. Cer. Soc.*, 7, 379, 1924.

[2] These samples were selected because they were clear and free from any visible signs of weathering.

[3] J. W. Mellor, *Trans. Cer. Soc.*, 9, 94, 1910. See page 108.

than 10 per cent. of felspar, "the total error introduced by the decomposition of felspar by the sulphuric acid treatment does not exceed 0·2 per cent." under the conditions of his experiments, which were not very different from those mentioned above. Sabeck's results agree with those obtained by Seger (2·24 per cent. dissolved) and Jackson (2·24), but Langenbeck's figure was 17·3 per cent.[1] It might be thought that fig. 160 makes it questionable if Sabeck's argument is sound, because many of the felspathic grains in felspathic clays may be finer than can be obtained by artificial grinding, although it is probable that, if felspar so finely divided were deposited with the original clay, it would have weathered or changed comparatively quickly.

There is some uncertainty as to the composition of the particular felspar or felspars in a given clay. It is not easy to get felspar free from symptoms of weathering, for even the so-called clear crystals are usually affected. Much more then is it probable that the felspathic grains in clays will be more or less weathered. Weathered felspar dissolves rapidly in sulphuric acid. Consequently, it is not surprising to find results so divergent as 2·24 (Seger) and 17·3 (Langenbeck), even when the conditions of
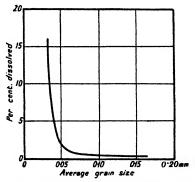
FIG. 160.—Effect of Grain Size on the Solubility of Potash Felspar.

the experiment and the degree of fineness of the felspar undergoing treatment are the same.

The attack is largely determined by the concentration of the different reagents, as well as the duration and temperature of the digestion in the acid-alkali treatment. It is therefore necessary to arrange conditions such that the felspar is affected as little as possible. It is a disadvantage to have the sulphuric acid too dilute, for it will then change considerably in volume during the digestion and particles of the clay may be left on the sides of the dish, as water evaporates, and consequently remain unattacked.[2] Sufficient acid must also be present to ensure the decomposition of all the argillaceous matters.

2. *Mica, Nepheline and Hornblende.*—If mica be present in the clay, as it usually is, it will be more or less attacked by the treatment. Some varieties of mica—phlogopite, for instance—will be almost completely decomposed along with the kaolinite. As in the case of felspar, the experimental evidence shows that the attack is dependent upon the type of mica present in the clay, the concentration of the reagents, the time of heating and the state of subdivision of the mica. Here are some results with selected samples of mica treated by the same process as that used for the felspars:—

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[1] H. Rose, *Scherer's Journ.*, 8, 233, 1803; H. A. Seger, *Notizblatt*, 12, 245, 1876; *Gesammelte Schriften*, Berlin, 42, 1896; Easton, Pa., 1, 53, 1902; K. Langenbeck, *The Chemistry of Pottery*, Easton, Pa., 9, 1895; W. Jackson and E. M. Rich, *Journ. Soc. Chem. Ind.*, 19, 1087, 1900; A. Sabeck, *Chem. Ind.*, 25, 90, 1902; J. Burian and J. Juránek, *Chem. Listy*, 1, 1912; *Silikat-Zeit.*, 2, 12, 1914; J. Splichal, *Jahrb. Min.*, (1), ref. 12–15, 1914; *Abh. böhm. Akad.*, No. 12, 1, 1913; R. Fresenius, *Anleitung zur quantitativen chemischen Analyse*, Braunschweig, 2, 352, 1877.

[2] C. Bischof (1884) and H. Hecht (1895) recommended an acid 1 : 6; H. A. Seger (1875), C. Bischof (1904), G. Lunge (1908) and A. Sabeck (1903), 1 : 3; H. A. Seger (1893), A. Leopold (1905) and E. Berdel (1903), 1 : 2; and B. Zschokke (1902), 1 : 1.

Effect of Rational Analysis on Mica (per cent. dissolved).

Size of grain (average diameter, mm.).	Muscovite. Clérmont Ferrant (Auvergne).	Lepidolite. Rozna (Mähren).	Biotite. Miask (Ural).	Phlogopite. Ontario (Canada).
Coarse—0·087 .	54·94	67·94	71·07	88·00
Fine—0·040 . .	55·56	70·02 [1]	92·50 [2]	93·93

This shows that mica is rapidly attacked by the method of rational analysis and part will be found in the soluble portion and part with the insoluble residue left after the treatment.

It might be added that similar experiments with a sample of hornblende from Moravicza (Austria) and a sample of nepheline from Vesuvius (Italy) gave:

	Coarse.	Fine.
Hornblende dissolved . .	1·79 per cent.	15·09 per cent.
Nepheline dissolved . .	98·63 ,,	99·62 ,,

3. *Quartz.*—The acids appear to have no appreciable effect on the quartz,[3] but quartz is affected by the caustic soda treatment. Brongniart and Malaguti substituted a solution of caustic soda for Forchhammer's sodium carbonate. The action of caustic soda on quartz has been studied in some detail. Michaelis,[4] in opposition to earlier workers, maintained that quartz is not appreciably affected when digested on a water bath with a 10 or 15 per cent. solution of caustic soda. This observation also contradicts the later work of Lemberg and Rinne,[5] who have shown that finely divided quartz is readily dissolved by this treatment. We must therefore assume that Michaelis was dealing with comparatively coarse grains of quartz, which are fairly resistant. Lunge and Millberg have shown that the solubility of quartz depends upon the fineness of the particles, the concentration of the reagent and the time of heating—*e.g.* a 15 per cent. solution of caustic potash dissolves from 1·0 to 1·5 per cent. of finely divided quartz in an hour's digestion, and 1·8 to 2·0 per cent. after

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[1] Another sample gave respectively 46·3 and 48·2 per cent.

[2] Another sample gave 60·97 and 89·2 per cent. respectively.

[3] See M. Wunder and A. Suleimann (*Ann. Chim. anal.*, **19**, 45, 1914) for the solubility of free silica in mineral acids. For the petrographic determination of free silica, see A. Rosiwal, *Verh. geol. Reichsanst. Wien*, 143, 1898; L. Schaetzer, *Céramique*, **29**, 301, 1926; A. Knopf, *U.S. Public Health Rep.*, **48**, 183, 1933; H. L. Ross and F. W. Sehl, *Ind. Eng. Chem. Anal. Ed.*, **7**, 30, 1935; S. H. Shaw, *Inst. Min. Met. Bull.*, **385**, 19, 1936; **386**, 9, 1936; **391**, 27, 1937.

[4] W. Michaelis, *Chem. Ztg.*, **19**, 1422, 2002, 2296, 1895; C. Rammelsberg, *Pogg. Ann.*, **112**, 182, 1861; J. N. Fuchs, *ib.*, **31**, 577, 1834; G. Jenzsch, *ib.*, **126**, 497, 1865; T. Scheerer, *Berg. Hütt. Ztg.*, **14**, 107, 1858; O. Maschke, *Zeit. deut. geol. Ges.*, **7**, 438, 1855; A. Müller, *Journ. prakt. Chem.*, (1), **98**, 14, 1866; R. Fresenius, *Anleitung zur quantitativen chemischen Analyse*, Braunschweig, **1**, 207, 1873; **2**, 338, 1877; H. Rose, *Handbuch der analytischen Chemie*, Leipzig, **1**, 751, 1851.

[5] J. Lemberg, *Zeit. deut. geol. Ges.*, **35**, 560, 1883; F. Rinne, *Zentr. Min.*, **334**, 1904; E. Kaiser, *Verh. nat. Ver. preuss. Rheinlande*, **54**, 93, 1897; *Zeit. Kryst.*, **33**, 200, 1900; A. Sabeck, *Chem. Ind.*, **25**, 90, 1902; B. Zschokke, *Baumaterialienkunde*, **7**, 165, 1902; *Mitt. Eidg. Materialprüf. Anstalt*, Zurich, **11**, 22, 1907; G. Lunge and M. Schochor-Tscherny, *Zeit. angew. Chem.*, **7**, 485, 1894; **8**, 593, 689, 1895; G. Lunge and C. Millberg, *ib.*, **10**, 393, 425, 1897; P. Kreiling, G. Lunge's *Methods of Chemical Analysis*, London, **1**, ii, 585, 1908; A. C. Rammelsberg, *Pogg. Ann.*, **112**, 117, 1861; H. Rose, *ib.*, **108**, 1, 1859; A. Steopoe, *Bul. Chim. pura appl.*, Bukarest, **32**, 37, 1930; **33**, 11, 1931; *Chem. Zentr.*, (1), 710, 845, 1932; A. Stassens, *15me. Cong. Chim. Ind. (Bruxelles, 1935)*, 155, 1936.

two hours' digestion, under conditions where a 15 per cent. solution of sodium carbonate dissolved only mere traces of the quartz. The attack is nearly ten times more vigorous when the quartz is in an extremely fine state of division. The experiments indicated above were repeated on a sample of clear rock crystal and on a sample of flint from Dieppe (France). The results were:

Average diameter of grain	0·165 mm.	0·032 mm.
Rock crystal	0·96 per cent.	6·40 per cent.
Flint	2·52 ,,	12·10 ,,

The experimental evidence thus shows that quartz is appreciably attacked when the clay is digested with caustic soda in order to remove the so-called colloidal silica, or the silicic acids formed during the action of sulphuric acid. Naturally, if the caustic soda be sufficiently dilute and is only in contact with the quartz a short time, the action may be reduced to a negligible minimum [1]; but the minimum may be quite appreciable if the quartz in the clay be in a
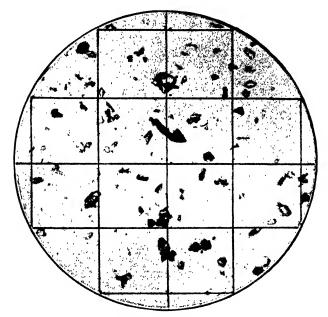
Fig. 161.—Residue obtained during the Rational Analysis of Shale. (× 1750.)

very fine state of subdivision. For this reason, Kreiling, and Lunge and Millberg, returned to the use of sodium carbonate as recommended by Forchhammer, in order that the quartz and felspar may be attacked as little as possible when the products of the action of the sulphuric acid are being removed.

Fig. 161 is a microphotograph of the residue obtained during the rational analysis of a sample of shale, and the sharp angularity of the grains shows that the attack, during the removal of the "argillaceous matter," was not very marked with the larger grains.

[1] A. Sabeck (l.c.) recommends a 2 per cent. solution of caustic soda; E. Berdel (Sprech., 36, 1483, 1903) a 6 to 7 per cent. solution.

§ 362. The Composition of the "Argillaceous Matter."

The term *Thonsubstanz* (clay substance) was applied by Senft [1] in 1867 to a hydrated aluminosilicate which is supposed to occur in all clays and to which they owe their plasticity. Senft's clay substance was what Brongniart and Malaguti called in 1840 *la véritable argile*; and other writers have expressed the same idea by the use of such terms as "ideal clay," "kaolinthon," (page 752). Aron and Seger applied the term to the finest fraction obtained in the elutriation of clays and also to the constituents decomposed by the action of concentrated sulphuric acid, thus implying that the clay substance in clays can be isolated or removed by both these processes. Kaolinite and clayite usually occur in an extremely fine state of subdivision and consequently accumulate in the finest fraction of the elutriation. But if, as is frequently the case, other finely divided constituents occur in the clay, they too will naturally collect in the fine fraction. These constituents may or may not behave like kaolinite when the clay is subjected to the acid-alkali treatment. Hence the use of the one term "clay substance" for totally distinct concepts must lead to confusion and misunderstanding.

Not only are kaolinite and clayite attacked by the acid-alkali treatment, but the felspar, mica and quartz, as well as pyrites, zeolites, fluorspar, hornblende, present in smaller proportions, are also attacked. It is therefore necessary to investigate the composition of the product of the reaction in question. The analyses of the argillaceous matter [2] in six different Cornish china clays on the market, dried at 110°, gave the following data:

Percentage Composition of the Argillaceous Matter of China Clays.

	Maximum.	Minimum.	Mean of six.	Ideal clay, $Al_2O_3 . 2SiO_2 . 2H_2O$.
Silica (SiO_2)	46·37	45·14	45·6	46·54
Titanic oxide (TiO_2)	1·11	0·08	0·5	..
Alumina (Al_2O_3)	40·28	38·19	39·2	39·50
Ferric oxide (Fe_2O_3)	1·48	0·52	1·0	..
Magnesia (MgO)	1·28	0·10	0·2	..
Lime (CaO)	1·41	0·25	0·3	..
Potash (K_2O)	1·36	0·52	1·0	..
Soda (Na_2O)	0·80	0·11	0·4	..
Loss on ignition	14·12	11·03	12·5	13·96

These clays contained from 80 to 98 per cent. of "argillaceous matter." As a result of similar experiments on German clays, Seger [3] drew the obvious conclusion: *The main constituent of certain high-grade clays is dissolved by the sulphuric acid treatment, and it corresponds in composition with $Al_2O_3.2SiO_2.2H_2O$.* Clearly it is not fair to apply this generalisation to all the different types of clays, since with other less pure clays very great discrepancies occur—see the table below for an example.

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[1] F. Senft, *Die Steinschutt und Erdboden*, Berlin, 236, 1867.

[2] We here use the term "argillaceous matter" for that heterogeneous mixture removed by the acid-alkali treatment.

[3] R. Fresenius, *Journ. prakt. Chem.*, (1), **57**, 65, 1852; H. A. Seger, *Notizblatt*, **12**, 245, 286, 1876; C. Loeser, *Kritische Beachtung einiger Untersuchungsmethoden der Kaoline und Thone*, Halle a. S., 18, 1905; *Tonind. Ztg.*, **32**, 1932, 1908.

Since the argillaceous matter includes the more important constituents of clay—rarely falling below 50 per cent. of the total constituents and sometimes ranging up to 99 per cent.—it is almost as important to get an idea of its mineralogical composition as it is of the clay itself. It is also better to use the general term "argillaceous matter" in preference to "clay substance," because the latter leaves the impression that we connote a substance $Al_2O_3.2SiO_2.2H_2O$, represented by analyses resembling those in the above table.

A Second Approximation to the Rational Analysis.—If the ultimate composition of the clay and of the fraction which resists the sulphuric acid treatment be determined, it is possible to compute numbers for the argillaceous and felspathic matters which are more promising than those given by the method of page 754. The data for Altofts' shale are given in the following table:

Analyses of Altofts' Shale.

	Ultimate analysis.		
	Total.	Residue.	Argillaceous matter.
Silica	51·92	38·77	13·15
Titanic oxide . . .	0·87	0·04	0·83
Alumina	20·08	0·88	19·20
Ferric oxide . . .	6·40	0·06	6·34
Magnesia	1·58	0·01	1·57
Lime	0·57	0·01	0·56 } 10·81
Potash	2·72	0·83	1·89
Soda	0·86	0·41	0·45
Loss on ignition . .	14·61	0·00	14·61
Totals . . .	99·61	41·01	58·60

The residue (column 3) is assumed to be composed exclusively of quartz and felspathic detritus. In typical potash felspar, $K_2O.Al_2O_3.6SiO_2$, one part of potash corresponds with 3·82 of silica; and in typical soda felspar, $Na_2O.Al_2O_3.6SiO_2$, one part of soda corresponds with 5·81 parts of silica. Hence,

Silica in felspar $= (0·83 \times 3·82) + (0·41 \times 5·81) = 5·55$ per cent.

The difference between this silica and the total silica in the residue represents the quartz. Hence, $38·77 - 5·55 = 33·22$ per cent. of free quartz and the percentage of felspar will be given by the balance, *i.e.* $41·01 - 33·22 = 7·79$. For the reasons given on page 755, we know that the argillaceous matter is contaminated with carbon and siderite. Hence, we must subtract 4·4 per cent. of carbon and 6·4 per cent. of siderite. This leaves $58·60 - 4·4 - 6·4 = 47·8$ per cent. of argillaceous matter. This gives:

Carbon . . . . . . 4·4 per cent.
Ferrous carbonate . . . . 6·4 „
Argillaceous matter . . . . 47·8 „
Felspathic detritus . . . . 7·8 „
Quartz . . . . . . 33·2 „

which should be compared with the result obtained experimentally on page 757.

Computation of the Amount of Mica in the Argillaceous Matter.—We have seen rational analyses of one clay from French and German laboratories reported in terms of clay substance, mica and quartz in the former case, and of clay substance, felspar and quartz in the latter. Some regularly assume that the argillaceous matter contains kaolinite or clayite and mica. Given the ultimate composition of the argillaceous matter, it is sometimes but not always possible to calculate the corresponding proportions of mica and kaolinite or clayite. An average mica is taken to be:

Silica	46·2	per cent.
Alumina	40·2	,,
Fluxes (Fe_2O_3, MgO, CaO, K_2O, Na_2O) . .	12·5 to 11·2	,,
Water	2·4	,,

Here, 11·2 to 12·5 of fluxes represent 100 parts of mica, or 1 of fluxes represents about 8·4 parts of mica. Given, therefore, a clay whose ultimate composition is that represented in the second column of the table on page 763, and the ultimate composition of the residue left by the sulphuric acid treatment that represented in the third column, the mica can be calculated as follows:—

The difference between the ultimate composition of the residue and of the whole clay obviously represents the composition of the argillaceous matter. This is shown in the last column of the above table.[1] The iron belonging to the ferrous carbonate is here included with the fluxes, which by hypothesis are associated with the argillaceous matter as mica. Now one part of ferrous carbonate corresponds with 0·69 part of ferric oxide, hence $6·4 \times 0·69 = 4·4$ parts of ferric oxide must be deducted from the fluxes. This leaves $(10·8 - 4·4) = 6·4$ per cent. of fluxes. Multiply the total amount of the fluxes, 6·4, in the argillaceous matter by 8·4, as indicated above. The result:

$$\text{Mica in argillaceous matter} = 6·4 \times 8·4 = 53·8 \text{ per cent.}$$

Subtract this number, 53·8, from 47·8, and we get an absurd result. This means that *the fundamental assumption that the fluxes in the argillaceous matter are wholly derived from mica is false.*

With some clays the results seem to be satisfactory, and the method was used extensively by Vogt[2] and by Lavezard in their studies on the clays of France. We have considered it better to give a failure rather than to select a clay with which the process is more or less satisfactory. There must always be a considerable amount of uncertainty owing to our ignorance of the particular type of mica in the given clay. A clay containing much mica may appear not unlike kaolinite in composition when the alkalies are computed to mica. One feature in the calculation is that it reveals how investigators, dissatisfied with Seger's method of rational analysis, are groping for further light on this subject. Virtually we have tried rationally to analyse the results of a rational analysis, and failed.

Leopold's Process of Rational Analysis.—This leads us to Leopold's method of conducting the rational analysis,[3] which has been used in a modified form

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[1] The microscopic examination of a clay will generally show the presence or absence of mica—usually the former.

[2] G. Vogt, *Bull. Soc. d'Encour. l'Ind. nat.*, (5), **2**, 633, 1897; *Contribution à l'Étude des Argiles et de la Céramique*, Paris, 193, 1906; E. Lavezard, *ib.*, 113, 1906; E. Berdel, *Sprech.*, **36**, 1483, 1903; O. Kallauner and J. Matejka, *ib.*, **47**, 423, 1914. For a comparison of Kallauner's and Seger's methods, see W. F. Fisher, *Journ. Amer. Cer. Soc.*, **11**, 842, 1928; K. Langenbeck, *The Chemistry of Pottery*, Easton, Pa., 9, 1895.

[3] A. Leopold, *Magyar Chem. Folyoirait*, **11**, 117, 1905; H. Bollenbach, *Chem. Ind.*, **31**, 445, 1908; *Sprech.*, **41**, 340, 351, 1908; E. Greiner, *ib.*, **42**, 399, 413, 1909; W. Cronquist, *Oester. Zeit. Berg. Hütt.*, **47**, 522, 1899; B. von Horváth, *Zeit. anal. Chem.*, **55**, 513, 1916.

by others. After digesting the clay with sulphuric acid and water in the usual way, instead of treating the residue with alkali, Leopold dilutes the contents of the basin with water; cools; adds ammonia until the solution reacts alkaline; filters; washes with hot water; dissolves the precipitate off the filter-paper in hydrochloric acid, washes the residue, and makes the filtrate and washings up to 250 c.c. with water. The alumina, iron oxide and lime are determined in aliquot portions of this solution. Multiply the amounts of alumina by 2·532 to get the kaolinite; the iron oxide can be calculated to Fe_2O_3, or to nontronite, $Fe_2O_3.3SiO_2.5H_2O$; the lime may be computed as if it were gypsum, if the ultimate analysis shows this mineral is present in appreciable quantities; the alkalies in the filtrate from the alumina precipitate are calculated to muscovite; and the alkalies in the residue on the filter-paper, after the removal of the ammonia precipitate, are calculated to felspar.

These methods are highly artificial, and the results are affected by an uncomfortable number of assumptions. The pseudonym "rational analysis" has misled many to believe that the results are as trustworthy as, or even more trustworthy than, those given by a regular ultimate analysis. Sometimes, in fact, the rational analysis appears to be highly irrational. The truth is that in some cases the rational analysis is accurate, valuable and useful; in others, it is inaccurate, misleading and false.

§ 363. Free, Combined and Colloidal Silica.

If the clay under investigation contains colloidal silica, most of this will pass into solution when the clay is digested with acid, and all will dissolve when the argillaceous matter is determined. Colloidal silica, if not separately determined, will then be reported with the argillaceous matter.[1] Some consider that a small quantity of colloidal silica has an important influence on the working properties of the clay. This question, however, is not, at present, under discussion.

The Determination of Colloidal Silica.—The colloidal silica in a clay can be determined by digesting 2 grms. of the sample with 100 c.c. of a 5 per cent. solution of sodium carbonate in a platinum dish on a water bath for about an hour. Decant off the clear liquid through a filter-paper[2] and repeat the treatment with fresh solution. Filter off the residue and wash with a hot dilute solution of sodium carbonate. Add an excess of hydrochloric acid to the filtrate; evaporate to dryness and separate the silica as described on page 147. Or, the residue can be washed, dried and weighed—the "loss" represents the matter removed by the sodium carbonate treatment,[3] and will include

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[1] W. H. Zimmer, *Trans. Amer. Cer. Soc.*, 3, 25, 1901; F. G. Pence, *ib.*, 12, 43, 1910. A. Hambloch (*Chem. Ztg.*, 36, 1058, 1912) uses a 5 per cent. sodium hydroxide solution and points out that other substances besides silica may be dissolved. E. Manzella (*Ann. Chim. appl.*, 1, 222, 1914) considers treatment with sodium hydroxide solution useless for discriminating between the various forms of amorphous and crystalline silica, since successive extractions with the lye result in the continued dissolution of the silica. J. M. van Bemmelen (*Zeit. anorg. Chem.*, 22, 313, 1900; *Landw. Vers. Stat.*, 37, 279, 1890) recommends a solution of potassium hydroxide of specific gravity 1·05 acting for 5 minutes at 50°. B. von Horváth (*Bied. Zentr.*, 47, 97, 1918) digests 5 grms. of the sample with 100 c.c. of one per cent. sodium carbonate for 15 minutes at 100° C.

[2] Care must be taken in filtration, since small particles of clay may pass through ordinary filter-papers.

[3] R. Fresenius, *Journ. prakt. Chem.*, (1), 57, 65, 1852; *Anleitung zur quantitativen chemischen Analyse*, Braunschweig; Eng. trans., London, 2, 269, 1900; C. F. Rammelsberg, *Pogg. Ann.*, 112, 177, 1861; W. F. Hillebrand, *Bull. U.S. Geol. Sur.*, 176, 109, 1900; F. H. Hatch, *Tschermak's Mitt.*, 7, 308, 1886; A. J. J. Browne and J. B. Harrison, *Quart. Journ. Geol. Soc.*, 48, 170, 1892; F. G. Pence, *Trans. Amer. Cer. Soc.*, 12, 43, 1910.

much of the colloidal alumina, if present, which will consequently be reported with the colloidal silica.

The Results.—It is advisable to run a blank experiment and to keep the stock solution of sodium carbonate in a ceresine bottle, because, as previously indicated, a solution of sodium carbonate removes silica from glass and porcelain vessels. To illustrate the results obtained by this process the following determinations are cited (all but the first number have been corrected by subtracting the "correction factor" 0·02):

	Per cent. dissolved.
Blank experiment (or correction factor) . .	0·02
Silicic acid (precipitated and dried at 110°) . .	100·00
Silicic acid (ignited 20 minutes on blast) . .	75·62
Quartz (rock crystal)—coarse (page 761) [1] .	0·11
Quartz (rock crystal)—fine (page 761) [1] .	1·23
Quartz sand (ignited 20 minutes on blast) [1] .	1·78
Altofts' shale	1·48
Glenboig clay	2·08
Halloysite (Vigoux, Indre).	10·58

If no allowance is made, there is therefore a small error due to the action of the sodium carbonate solution on quartz. We are not sure if the sodium carbonate removes all the colloidal silica. The error is much greater if the sodium carbonate solution be mixed with sodium hydroxide, as in Lunge's solution.

Other Methods.—Sjollema [2] claims that far more accurate results are obtained by boiling the sample with a 33 per cent. aqueous solution of diethylamine. Apart from the cost of the reagent, and the fact that the solution bumps badly when boiling, rather poor results have been obtained in our experience with this process. Hermann [3] recommends boiling the clay with a 0·1 per cent. solution of potassium paratungstate. When 10 c.c. of the solution are afterwards treated with 1 c.c. of an aqueous solution of sodium acetate [4] and 3 drops of a 5 per cent. solution of cæsium chloride, a crystalline precipitate is obtained if colloidal silica be present. The process has not proved satisfactory when it is applied quantitatively. In the absence of phosphoric acid, the molybdate process (page 686) can sometimes be used for determining the amount of silica in the extract from the clay.[5]

Free and Combined Silica.—Some analysts apply the term *combined silica* to the silica present in that portion of a clay which is decomposed by the sulphuric acid treatment; and the term *free silica* to the silica present in that portion of the clay which is not decomposed by the sulphuric acid treatment. The idea seems to be that the clay is composed of kaolinite and sand or quartz; that kaolinite alone is broken down by the sulphuric acid treatment; and that

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[1] According to R. Schwarz (*Zeit. anorg. Chem.*, 76, 422, 1912), when grains 0·04 mm. in diameter are boiled for half an hour with a 5 per cent. solution of sodium carbonate, 2·11 per cent. of quartz dissolves; and 2·77 per cent. of tridymite. For the solubility of silica in 1 per cent. sodium hydrocarbonate solution, see E. J. King, *Nature*, 140, 320, 1937.

[2] B. Sjollema, *Journ. Landw. Chem.*, 50, 371, 1902.

[3] H. Hermann, *Zeit. anal. Chem.*, 46, 318, 1907.

[4] Dissolve 15 grms. of crystalline sodium acetate in 35 grms. of water and 5 c.c. of glacial acetic acid.

[5] For recent work on the colorimetric determination of silica, see E. J. King and C. C. Lucas, *Journ. Amer. Chem. Soc.*, 50, 2395, 1928; R. J. Robinson and H. J. Spoor, *Ind. Eng. Chem. Anal. Ed.*, 8, 455, 1936; F. De Eds and C. W. Eddy, *Journ. Biol. Chem.*, 114, 667, 1936; A. R. Tourky and D. H. Bangham, *Nature*, 138, 587, 1936; I. P. Alimarin and V. S. Zverev, *Mikrochem.*, 22, 89, 1937.

...ne insoluble matter is sand or free silica.[1] All three assumptions are erroneous. Further, the insoluble residue includes various silicates—*e.g.* felspar, mica, hornblende, and in these silicates, the silica, SiO_2, is just as much "combined" as that combined in the kaolinite. Hence, the objections urged against the system of rational analysis might also be advanced here; and Ries rightly argues that the custom of reporting the "silica" as "free silica" and "combined silica" should be dropped, because the terms are misleading.[2]

§ 364. The Composition of Felspathic and Quartz Detritus.

We next investigate the composition of the residue left after the clay substance has been removed. Following Seger, it is generally assumed that the residue is unweathered felspar or felspathic minerals and quartz. This assumption, in many cases, has no experimental foundation. For instance, felspar is seldom, if ever, found in the china clay from Cornwall or Devonshire, and yet half the residue in these clays would be reported as felspar by the method of rational analysis. Hussak, also, found no felspar in the majority of the kaolins he examined.[3] In spite of this, it is by no means uncommon to find ball and china clays reported with p per cent. of felspar when none is present.

The felspathic residue will include all those minerals which resi -, wholly or in part, the sulphuric acid treatment. Again, practically all ' iliceous minerals are decomposed by hydrofluoric acid, but as indicate '· 753, a few less important minerals will escape that acid, and, in con: 'iese will be included with "quartz *débris.*"

Again, the mixed oxides of aluminium and iron are su[... alumina, and, on that assumption, their weight is multiplied by 5·4...—the amount of potash felspar corresponding with one part of alumina. Usually, a part of the potash in the ideal potash felspar is replaced by soda, and a part of the aluminium by iron. Both these factors make the above ratio deviate from 5·459. Seger used 5·41. Bollenbach[4] determines the ferric oxide separately and subtracts it from the "ammonia precipitate" before basing any calculations on the R_2O_3 oxides. Others[5] have multiplied the amount of the fluxes by 9, or by 8·5, and called the felspathic detritus "mica." We have seen on page 760 that a part of the mica in the clay may appear with the argillaceous matter and part with the felspathic detritus. In consequence, there is some uncertainty as to the nature of the minerals which make up the residue from the sulphuric acid treatment.

It is seldom possible to make a quantitative estimate from the microscopic

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[1] See T. E. Thorpe, *Quantitative Chemical Analysis*, London, 184, 1903.

[2] H. Ries, *Clays—their Occurrence, Properties, and Uses*, New York, 68, 1906. W. R. Line and P. W. Aradine (*Ind. Eng. Chem. Anal. Ed.*, 9, 60, 1937) report that fluoboric acid decomposes silicates but has little or no effect on quartz. E. Chauvenet, P. Avrard and J. Boulenger (*IX Cong. inter. Quim. pura apl.*, 6, 222, 1936) heat the powdered mineral in a current of carbon tetrachloride at 900°–930°, when all substances, except free silica, are changed to volatile or water-soluble chlorides. These observations suggest the possibility of the direct determination of quartz in clays.

[3] E. Hussak, *Sprech.*, **22**, 8, 1889.

[4] H. Bollenbach, *Sprech.*, **41**, 340, 351, 1908.

[5] A. E. Tucker (*The Great Western Railway Co. v. The Carpella United China Clay Co. Ltd.*, 175, 1908) and R. R. Tatlock (*The North British Railway Co. v. Turners Ltd.*, 74, 1904) consider calculating the alkalies to felspar to be the "fairest and best" way. Obviously, if we are satisfied with guessing, either way may be taken. See also W. C. Hancock, *Journ. Soc. Chem. Ind.*, **29**, 309, 1910.

examination of the clay, because: (1) The minerals are often covered with a more or less opaque weathered crust which prevents an application of the optical tests; and (2) The mineral grains are often too small to permit satisfactory optical tests.[1] Hence, the method of rational analysis has received but little, if any, aid from the microscope.

§ 365. The Ultimate and Rational Analyses.

Some have been so strongly impressed with the difficulties involved in conducting a satisfactory rational analysis that they have abandoned the operation,[2] and calculated the supposed mineral composition by a process similar to that which follows.

It is required to calculate the proportion of (1) *kaolinite or clayite,* (2) *felspar and* (3) *quartz on the assumption that the clay contains potash and soda felspars, quartz and clayite or kaolinite.* Several different ways are possible; not all are concordant.[3] Take Altofts' shale in illustration. The ultimate analysis of the sample of Altofts' shale, dried at 110°, previously cited, gave:

SiO$_2$	TiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	CaO	K$_2$O	Na$_2$O	Loss on ignition.
51·92	0·87	20·08	6·40	1·58	0·57	2·72	0·86	14·61

The loss on ignition included 4·42 per cent. of carbon, and 2·44 per cent. of carbon dioxide.

From the formulæ for potash (K$_2$O.Al$_2$O$_3$.6SiO$_2$) and soda (Na$_2$O.Al$_2$O$_3$.6SiO$_2$) it follows that the per cent. K$_2$O × 3·82 represents the per cent. of potash felspar; and the per cent. of Na$_2$O × 5·81 represents the silica in soda felspar. Hence, the amount of silica in the two will be:

Potash felspar   .   .   .   3·82 × 2·72 = 10·39 per cent.
Soda felspar   .   .   .   5·81 × 0·86 = 5·00   ,,
$\overline{}$ Total silica in the felspars .   .   15·39   ,,

Again, from the formulæ for the two felspars, the per cent. of potash multiplied by 1·08 represents the amount of alumina in potash felspar; and the per cent. of soda multiplied by 1·64 gives the corresponding amount of alumina in the soda felspar. Hence, the alumina in the two felspars will be:

Potash felspar   .   .   .   1·08 × 2·72 = 2·94 per cent.
Soda felspar   .   .   .   1·64 × 0·86 = 1·41   ,,
$\overline{}$ Total alumina in the felspars   .   4·35   ,,

The difference between the total alumina and the alumina in the felspars represents the alumina in the kaolinite; and the product of the alumina in the kaolinite with 1·18 represents the amount of silica combined as kaolinite. Hence—

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[1] Thus, a most experienced mineralogist reported that he was unable to say for certain whether some of the finer grains in the above-mentioned shale were mica or quartz. For the difficulty with mica and kaolinite, see J. W. Gregory, *The Great Western Railway Co. v. The Carpella United China Clay Co. Ltd.*, 324, 1908.

[2] E. R. Buckley, *Report on the Clays and the Clay Industries of Wisconsin*, Madison, Wis., 267, 1901. See also Heim, *Sprech.*, **28**, 519, 547, 1895; R. C. Purdy, *Trans. Amer. Cer. Soc.*, **14**, 301, 1912; G. S. Tilley and J. D. Sullivan, *Journ. Amer. Cer. Soc.*, **7**, 379, 1924; J. S. McDowell, *ib.*, **9**, 61, 1926; compare J. W. Mellor in *Collected Papers, County Pottery Lab. Staffordshire*, London, 109, 1914.

[3] For instance, if we make an assumption about the composition of the mica, felspar, clayite and quartz presumably in the clay, the method of calculation devised by J. W. Mellor, *Trans. Cer. Soc.*, **7**, 117, 1908, can be used after deducting the proper allowance for siderite and carbon.

Alumina in clay . . . . . 20·08 per cent.
Alumina in felspars . . . . 4·35 ,,

Alumina in kaolinite . . . 15·73 ,,

The ferric oxide presents a difficulty. Is it to be ignored? Is it to be included with the "alumina"? Is it to be calculated as nontronite—Fe_2O_3. $3SiO_2.5H_2O$? Or is it to be included with the clay substance? With high-grade china clays there is no difficulty in answering the questions, because the amount of iron is negligibly small—so far as the degree of accuracy of the calculation is concerned. It is usually included either with the alumina or with the argillaceous matter, generally the latter. As a matter of fact, in this particular sample most of the iron was removed by digestion with hydrochloric acid (1 : 1), and it should therefore be placed as a constituent by itself. The fact that the clay effervesced with evolution of carbon dioxide when treated with an acid proved that some constituents in the ultimate analysis were present as carbonate. The comparatively low proportion of lime and magnesia and the high proportion of "iron" pointed to the presence of ferrous carbonate. When the necessary calculation is made, we get: Per cent. of carbon dioxide × 1·63 = 2·44 × 1·63 = 3·98 per cent of FeO; or 3·98 + 2·44 = 6·42 per cent. of ferrous carbonate. Hence, since: Per cent. of ferrous oxide × 1·11 = 3·98 × 1·11 = 4·42 per cent. of ferric oxide, 6·40 − 4·42 = 1·98 per cent. of ferric oxide remains unaccounted for. Again,

Silica with kaolinite (1·18 × 15·73) . . 18·56 per cent.
Silica with felspars . . . . 15·39 ,,

Silica with kaolinite and felspars . . 33·95 ,,

Total silica in clay . . . . 51·92 per cent.
Silica with kaolinite and felspars . . 33·95 ,,

Silica as quartz . . . . 17·97 ,,

Add up the percentage amounts of titanic oxide, magnesia,[2] lime and alkalies, with the computed amounts of silica and alumina for the felspars; and add up the loss on ignition less carbon (4·42) and carbon dioxide (2·44), ferric oxide and the computed alumina and silica for the kaolinite as argillaceous matter.[3] Summarising these results:

Argillaceous matter	Silica	18·56	
	Alumina and iron oxide	17·71	44·02
	Water	7·75	
Felspathic matter	Silica	15·39	
	Alumina	4·35	26·34
	Bases	6·60	
Quartz (silica)			17·97
Ferrous carbonate			6·42
Carbonaceous matter			4·42

[1] We have seen, page 755, that most of the iron in this particular shale was probably present as ferrous carbonate.

[2] If calcium and magnesium carbonates were present, they would be removed by the hydrochloric acid treatment.

[3] The loss on ignition may be used as a check on the work, since the product of the loss on ignition with 7·16 represents the corresponding amount of clayite or kaolinite. This product is usually rather less than the actual amount of clayite, particularly if the carbonaceous matter and carbon dioxide be first deducted. There is a small error due to gain in weight by the oxidation of ferrous oxide. Some consider that the water in the clayite, $Al_2O_3.2SiO_2.2H_2O$, is to some extent replaced by alkali oxide. C. F. Binns (*Trans. Amer. Cer. Soc.*, 8, 198, 1906) assumes that a little of the alkali is adsorbed by the argillaceous matter.

A comparison of this with the rational analysis, as indicated in the table below, is not satisfactory. The discrepancy partly arises from the *dubious assumption* that the alkalies in the ultimate analysis all belong to felspathic matter and

Comparison of the Rational Composition of Aftofts' Shale Estimated [1] by Different Methods.

	Rational analysis.	Computed from ultimate analysis of matter soluble and insoluble in sulphuric acid, etc.	Computed from ultimate analysis of whole clay.
Carbonaceous matter .	4·4	4·4	4·4
Ferrous carbonate .	6·4	6·4	6·4
Argillaceous matter .	48·6	47·8	44·0
Felspathic detritus .	5·4	7·8	26·3
Quartz *débris* . .	35·2	33·2	18·0

none to micaceous and argillaceous matters. The method here outlined generally gives good results with high-grade clays, but with the low-grade clays, as with the rational analysis proper, the results are hopeless. Consequently, our attitude towards the method of calculation just indicated, and to the process of rational analysis, is largely determined by the particular type of clay under consideration and the purpose for which the estimation is made. With the high-grade clays, the margin of error is small; with low-grade clays (and possibly with Cornish stone), we can say with Bischof [2] the process is "worthless" (*wertlos*), and with Prössel, "useless" (*unbrauchbar*).

We must here confess our inability to prescribe a process of chemical analysis of general applicability which will enable us to deduce the exact mineralogical composition of clays. *Blind faith in the routine process is sure to err.* A certain amount of judgment must be exercised in adapting a process of analysis to particular clays and to particular methods of manufacture. We must decide what minerals are technically important, and a process must be devised to deal with them, not necessarily to furnish the highest degree of accuracy, but rather to serve as a guide for the best treatment of the clay to give the desired results. One example will suffice.

schokke's Method of Rational Analysis.—Zschokke [3] found the following combined mechanical and chemical process best suited his requirements:

(1) Boil 50 grms. of the dry clay for half an hour in a porcelain dish with water and restore the water lost by evaporation from time to time. After standing 24 hours, wash the clay on a sieve 8570 Continental mesh (say, 240 British mesh) until the washings flow through clear. Break up any lumps by

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[1] Note the distinction between *to estimate* and *to determine* in analytical work. The former means "to judge or form an opinion from imperfect data"; the latter, "to ascertain by definite measurement." Sometimes it is difficult to decide where to draw the line—*e.g.* soda, page 235, § 110; and sometimes an estimation is more accurate than a determination. However, the distinction has been emphasised in the Courts.

[2] C. Bischof, *Die feuerfesten Tone*, Leipzig, 103, 1904; B. P. Tenax (B. Prössel), *Die Steingut und Porzellanfabrikation*, Leipzig, 8, 1879.

[3] B. Zschokke, *Baumaterialienkunde*, 7, 165, 1902; *Mitt. Eidg. Materialprüf. Anstalt*, Zürich, 11, 22, 1907.

rubbing on the sieve or between the fingers or, if necessary, on a glass plate with a rubber pestle. The residue on the sieve consists of coarse-grained quartz, felspar, calcium and magnesium carbonates, (gypsum, pyrites). Dry at 110° and weigh.

(2) The residue on the sieve is treated with dilute hydrochloric acid (1 : 10) filtered and washed until the washings show no reaction for lime. Dry and weigh the residue. The weight of the residue gives the weight of the coarse grained quartz and felspar, (pyrites).

(3) The washings from (1) are evaporated to dryness and weighed. The result is fine-grained quartz, felspar, calcium and magnesium carbonates, (gypsum, pyrites), and soluble salts, if any.

(4) Treat the residue from (3) as described under (2). The weight of the acid-insoluble residue gives the weight of the fine-grained quartz and felspar, (pyrites).

The results are expressed in percentages:

I. Non-plastic constituents . . . . . . 38·6
    A. Coarse-grained constituents . . . 13·9
        (a) Quartz, felspar . . . . 7·8
        (b) $CaCO_3$ and $MgCO_3$ . . . 6·1
    B. Fine-grained constituents . . . . 24·7
        (a) Quartz, felspar . . . 11·3
        (b) $CaCO_3$ and $MgCO_3$ . . . 13·4
II. Clay substance (by difference) . . . . . 61·4

The clays treated by this method were required for bricks fired at too low a temperature for the felspar and quartz to play a particularly important part during the firing. Information about the size of grain of the non-plastic constituents and the amount of the calcium and magnesium carbonates present in the clay was particularly desired. Hence a justification of Zschokke's procedure.

§ 366. Are the Ultimate and Rational Analyses Consistent ?

The ultimate and rational analyses of the high-grade clays, that is, clays containing a large proportion of kaolinite or clayite, usually agree very well. With these clays the proportion of felspar and quartz detritus is small. Consequently, the errors arising from secondary reactions in the removal of substance are relatively small. For instance, if a clay has , per cent argillaceous matter, 4 per cent. of felspar and 26 per cent. of quartz, even 20 per cent. of the felspar breaks down by the sulphuric acid treatment, would only have the effect of diminishing the proportion of felspar 0·8 per cent and of raising the clay substance accordingly. If two clays contain the same minerals and if the sulphuric acid attacks both in the same way, the ultimate and rational analyses must necessarily agree. Disagreement can only occur when the clays contain different minerals or the same minerals in different proportions or in different states of subdivision. Cases have been recorded which apparently contradict this observation. For example [1]:

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[1] A is a raw china clay from North Carolina—H. Ries, *North Carolina Geol. Sur.*, **13**, 62, 1897; B is a slip clay from Löthian, Saxony—H. A. Seger, *Tonind. Ztg.*, **16**, 1031, 1892; and C is a clay from Shropshire—J. T. Norman, *Report on Some Shropshire Clays*, London. 1903.

ULTIMATE ANALYSES.

	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O, Na_2O	Loss on ignition.
. . .	62·40	26·51	1·14	0·01	0·57	0·98	8·80
. . .	62·52	25·57	0·92	0·10	0·65	1·04	9·27
. . .	59·30	27·17	1·44	nil.	0·48	0·52	9·67

RATIONAL ANALYSES.

	Clay substance.	Felspar.	Quartz.
A	66·33	18·91	15·61
B	72·05	0·10	27·76
C	43·74	36·84	19·42

In A the proportion of alkalies to felspar is 1 : 19. We do not know any felspar with alk: :es and felspar in these proportions by weight. In albite the ratio is about 1 : 8 and in orthoclase, 1 : 6. There is obviously something wrong. The case is much worse with the C clay, for it is at once obvious that 0·52 per cent. of alkalies is quite incompatible with 36·8 per cent. of felspar. See also page 770. Such inconsistencies are not at all uncommon,[1] although we have not met such bad examples in our own practice. We are thus driven to conclude that the method gives incompatible results, or the analyses are at fault. We naturally inquire: Was the clay substance all decomposed by the sulphuric acid treatment in the rational analysis of clays A and C? Was some of the felspar decomposed by the sulphuric acid in the rational analysis of clay B?

Summary.—Here, then, it is inferred that the method for conducting the rational analysis gives results incompatible with the ultimate analysis; the ultimate analysis can be conducted with a great degree of precision; hence the process of rational analysis cannot be recommended as a general method for comparing the properties of the different types of clay, although, as indicated above, the rational analysis is useful (1) for comparing the properties of high-grade clays which do not differ very materially in the nature of their constituent minerals; and (2) it is sometimes a help in forming a rough idea of what minerals are present in clays.[2] In the former case, however, the "rational composition" can be computed accurately enough from the ultimate analysis.

. W. Mellor, *Pot. Gaz.*, **35**, 1060, 1908; H. Ries, *Trans. Amer. Inst. Min. Eng.*, **28**, 898.

Or rather the fractional separation of constituents soluble in certain menstrua.

Table LXVIII.—Solvents for Precipitates in Munroe's Crucible.

O. D. Swett, *Journ. Amer. Chem. Soc.*, **31**, 928, 1909.

(Salts are applied in aqueous solution unless otherwise specified.)

1. Water.
2. Alcohol.
3. Carbon disulphide.
4. Sulphuric acid with nitric acid or nitrates.
5. Sulphuric acid, concentrated or fuming, with ammonium chloride.
6. Nitric acid.
7. Carbon dioxide in aqueous solution.
8. Acetic acid.
9. Oxalic acid.
10. Hydrochloric acid with ammonium chloride or oxalic acid.
11. Hydrofluoric acid.
12. Potassium hydroxide.
13. Sodium hydroxide.
14. Ammonium hydroxide.
15. Potassium sulphide.
16. Potassium sulphide, yellow.
17. Sodium sulphide.
18. Sodium sulphide, yellow.
19. Ammonium sulphide.
20. Ammonium sulphide, yellow.
21. Potassium bisulphite.
22. Sodium thiosulphate.
23. Ammonium sulphate.
24. Ammonium nitrate.
25. Sodium hydrogen phosphate.
26. Ammonium oxalate.
27. Ammonium acetate, alkaline.
28. Ammonium tartrate, alkaline.
29. Potassium carbonate.
30. Sodium carbonate.
31. Potassium chlorate.
32. Ammonium carbonate.
33. Potassium chloride.
34. Potassium iodide.
35. Sodium chloride.
36. Ammonium chloride.
37. Ammonium fluoride, dry.
38. Calcium chloride.
39. Magnesium chloride.
40. Potassium cyanide.
41. Ferrous sulphate.
42. Silver nitrate.
43. Lead acetate.
44. Mercuric nitrate.
45. Ferric acetate.

Solvents for Precipitates in Condition for Weighing.

(Numbers indicate correspondingly numbered solvents in the preceding list. Hyphens indicate successive treatments ; commas indicate alternative treatments. Abbreviations : h = hot, c = concentrated, d = dilute.)

Precipitates.	Solvents	Precipitates.	Solvents.
Aluminium oxide .	12ch-1-10, 13ch-1-10	Barium chromate .	6, 10
Ammonium arseno-molybdate.	14.	Barium silicofluoride	36
		Barium sulphate .	4h, 5h
Ammonium chloride	1h.	Bismuth . .	6d
Ammonium magnes-ium arsenate.	6, 10.	Bismuth carbonate (basic).	6, 10
Ammonium phos-phomolybdate.	1h, 12, 13, 25, 26, 29, 30, 36	Bismuth chromate (basic).	6
Ammonium chloro-platinate.	1h	Bismuth nitrate (basic).	6
Antimony . .	6-1-10	Bismuth oxide .	10
Antimony pentasul-phide.	14h	Bismuth oxychloride	10c
		Bismuth sulphide .	6ch-1-3
Antimony tetroxide	10ch	Cadmium carbonate	6d, 14
Antimony trisul-phide.	10c, 12d, 15, 19	Cadmium oxide .	4, 5, 6, 10, 14
		Cadmium sulphide .	4dh, 6, 10
Arsenious sulphide .	12, 13, 15. 17, 21, 29, 30	Calcium carbonate .	6d, 10d
		Calcium carbonate, ignited.	1h, 6d, 10d
Barium carbonate .	7, 24, 36		
Barium carbonate, ignited.	1h, 6d	Calcium fluoride .	4-1, 10c
		Calcium oxalate .	6, 22

Table LXVIII.—*continued.*

Precipitates.	Solvents.	Precipitates.	Solvents.
Calcium sulphate	23dh	Mercuric oxide	6, 10
Chromium oxide	6ch + 31dry +42 or 43, 31dry h+1, 42dry h+6	Mercuric sulphide	15 ! 12
		Mercurous chloride	6ch-1
		Mercurous chromate	6ch
Cobalt	6	Mercurous phosphate	6
Cobalt hydroxide	23, 24, 36	Metastannic acid	10, 13
Cobaltous sulphate	1h	Nickel	6c
Cobaltous sulphide	4c, 5, 8c, 10c	Nickel oxide	10
Cupric hydroxide	6, 10, 14	Nickelous hydroxide	10d, 14, 23, 24, 36
Cupric sulphide	6h, 40	Nickelous subsul-phide	6
Cuprous oxide	4		
Cuprous sulphide	6	Nickelous sulphate	1h
Cuprous thiocyan-ate.	4	Nickelous sulphide	6
		Palladium iodide	14
Gold	4c	Platinum sulphide	16, 18
Gold sulphides	16, 40	Potassium chloride	1h
Iron acetate (basic)	10	Potassium cobaltic nitrite.	1h
Iron arsenate	6, 10		
Iron formate (basic)	10	Potassium fluoborate	1, 2d
Iron hydroxide	6d, 10d.	Potassium chloro-platinate.	1h, 12h
Iron oxide	10c		
Iron phosphate	10, 45	Potassium sulphate	1h
Iron succinate (basic)	4, 5, 6, 10	Silica	11, 12h, 13h, 29h, 30h, 37-ignition
Iron sulphide	4, 10		
Lead arsenate	6	Silver	6d
Lead carbonate	6d	Silver chloride	14h
Lead chloride	1h	Silver cyanide	14, 40
Lead chromate	6, 12	Silver iodide	34c, 22, 40, 44ch
Lead oxalate	6d	Silver phosphate	6, 14
Lead oxide	6d	Silver sulphide	6ch-1-3
Lead phosphate	6	Sodium carbonate	1h
Lead sulphate	24, 27, 28, 10ch, 6ch, 22, 12h, 13h, 14h	Sodium chloride	1h
		Sodium chloroplatin-ate.	1h, 2
Lead sulphide	6c, 10c	Sodium sulphate	1h
Magnesium oxide	4d, 6d, 10d	Stannic acid	10-1
Magnesium phos-phate.	6, 10	Stannic oxide	36dry-ignition, 10-1
		Stannic phosphate	12
Magnesium pyro-arsenate.	6, 10	Stannic sulphide (hydrous).	10ch, 12, 15, 17
Magnesium pyro-phosphate.	6, 8, 10, 6ch, 10ch	Stannous sulphide (hydrous).	10c
Magnesium sulphate	1h	Strontium carbonate	7, 24, 36
Manganese dioxide	5h ! 9	Strontium sulphate	33c, 35c, 38c, 39c
Manganese sesqui-oxide.	4 + 9, 4 + 41	Uranyl pyroarsenate	6
Manganese sulphide	4d, 6d, 10d	Uranyl pyrophos-phate.	4, 6, 10
Manganous pyro-phosphate.	4ch, 5h, 6ch, 10ch	Zinc oxide	10dh
Manganous sulphate	1	Zinc sulphide	4, 6, 10

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